Technologies and Processes for the Advancement of Materials

Thermal processing

ISSUE FOCUS ///

ADDITIVE MANUFACTURING / NITRIDING

ADVANTAGES OF WIRE-ARC ADDITIVE MANUFACTURING

COMPANY PROFILE ///

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FROM THE EDITOR ///

Carry on – good things are on the horizon

As we move into the fall of 2020, it finally looks like this insane year is waning, and, I think I speak for all of us — good riddance.

That doesn't mean a few good things haven't come out of the year. If nothing else, it has forced us to challenge our norms and readjust our way of thinking about almost every aspect of what we do and how we do it.

That being said, a lot of our quarantine time here at *Thermal Processing* has been devoted to brainstorming new and innovative ways to ensure you're getting the best and latest information about the companies supplying all your heat-treat needs.

We have quite a few irons in the fire, and we are hoping to be able to reveal them in the coming months. So, stay tuned.

One of *Thermal Processing's* disappointments in the wake of the COVID-19 pandemic is the fact that we won't be able to see any of you at FNA. It, as well as most trade shows for 2020, have either been canceled or postponed. But, thankfully, the people behind Furnaces North America have channeled all their show energy into producing a virtual version of FNA that promises to bring practically everything you would experience in person straight to the comfort of your computer monitor.

But don't take my word for it; check out my conversation with FNA show producer Tom Morrison about what you can expect from FNA's online trade show. It should make for a fascinating way to get your heat-treat show fix.

Whether tradeshows are virtual or postponed, let our September issue be your guide to a wide range of exciting developments in the industry.

In our cover article, I had the pleasure of talking with Dr. Mark Douglass with Lincoln Electric about a new technology — wire-arc additive manufacturing. This development allows for the 3D-printing of large and heavy metal objects, truly an amazing advancement in the burgeoning field of AM.

And new contributor Chris Wright shares his insights on whether nitriding can improve the corrosion and wear properties of additive manufactured stainless steel.

In addition to that, make sure you check out our company profile that features Graphite Metallizing Corporation and what the company's flagship product, GRAPHALLOY, can do to make your heat-treating requirements a little easier and more economical in the long run.

And before you dive into this month's issue, please take time to consider how *Thermal Processing* can also be your ally in getting your message to your customers. We offer many ways in which to remind the industry that your products and services are available.

That's good news for your audience in search of the very services and products that you can provide every day. And with the world trying to cope with economic and medical hardships, the deep reach *Thermal Processing* can provide is more important than ever.

I hope you enjoy this issue as much as I enjoyed putting it together. Keep diligent and stay safe, and, as always, thanks for reading!

KENNETH CARTER, EDITOR
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David C. Cooper
PRESIDENT

Teresa Cooper
OPERATIONS

This Grieve truck oven has 6-inch insulated walls, an aluminized steel interior, and aluminized steel exterior with enamel finish. (Courtesy: Grieve)

Grieve offers 550°F customized truck oven

This new Grieve oven is a 550°F (288°C) truck oven customized from the standard TCH-550 model and used for heat-processing parts at the customer's facility. Workspace dimensions of this oven measure 60" W x 60" D x 60" H. Also, 30 KW are installed in Incoloy-sheathed tubular heating elements, while a 2,000 CFM, 2 HP recirculating blower provides horizontal airflow to the workload.

This Grieve truck oven has 6-inch insulated walls, an aluminized steel interior, and aluminized steel exterior with enamel finish. Features include a purge timer, two-position dampers on fresh air inlet and exhaust outlet, and a 1,200-pound capacity stainless steel loading truck. Additional features include a 325 CFM powered forced exhauster with an airflow safety switch. The oven includes all safety equipment required by NFPA Standard 86, IRI, FM, and OSHA.

Controls on this Grieve oven include a UL-listed control panel, a programmable temperature controller, SCR power controller, a circular chart recorder, and a circuit breaker disconnect switch mounted through the control panel door.

MORE INFO www.grievecorp.com

Kemper offers stationary welding filter system

For cost-efficient entry into integral welding fume extraction, the new WallMaster filter system from Kemper lets metalworking companies optimize their protective welding equipment for employees. With an area of 42 square meters, the stationary unit has the largest filter surface in the entry-level price segment. Little effort is required to integrate and mount the unit behind extraction elements such as extraction arms or fans with no need for its own power supply. This also makes it suitable for simple retrofitting.

"Protecting employees from harmful welding fumes should not fail because of the costs of clean air technology," said Björn Kemper, chairman of the management board of Kemper GmbH. "The WallMaster means we are now closing the gap in the entry-level segment between low price barriers, effective filter technology and a space-saving product design."

The stationary filter unit is suitable for filtering medium quantities of welding fumes and dust at up to two workplaces simultaneously. The filter surface of 42 square meters is decisive in this respect. This is the highest capacity in the entry-level price segment of stationary welding fume extraction on the market to date. Users thus achieve significantly longer filter lives compared to conventional filter units. The WallMaster effectively separates even ultra-fine particles with a size of less than 0.1 µm to a degree of more than 99.5 percent.

The filter unit can be mounted on the hall wall, a pillar, or on a separately available stand, and its compact housing saves space in production areas. The WallMaster is easy to combine with collection devices from various manufacturers — for example, with one or two exhaust sets. It is even possible to retrofit the unit in existing collection devices.

"The WallMaster allows companies to expand their protective welding equipment from pure exhaust air to an effective air pollution control concept," said Kemper. "We are now creating a cost-effective expansion option for metal processors who previously managed without a filter in their welding

SEND US YOUR NEWS Companies wishing to submit materials for inclusion in Thermal Processing's Update section should contact the editor, Kenneth Carter, at editor@thermalprocessing.com. Releases accompanied by color images will be given first consideration.

Kemper's WallMaster, a wall-mounted unit with attractive price-performance ratio, SafeChangeFilter, and a system that can be retrofitted in existing extraction technology. (Courtesy: Kemper)

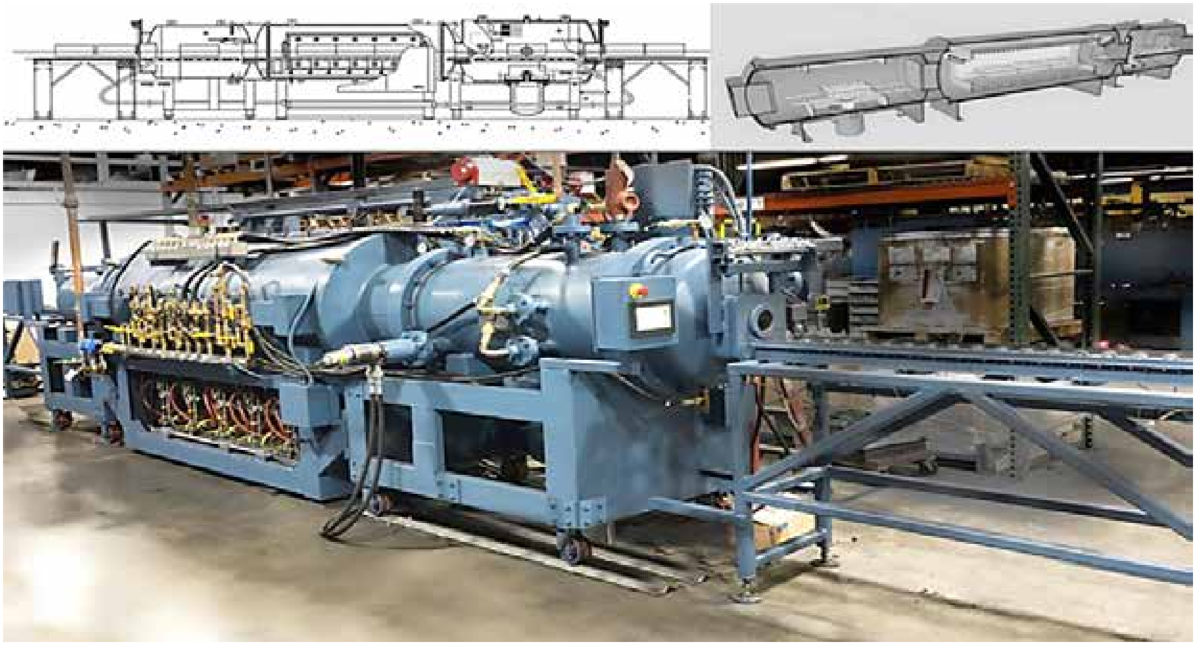
fume extraction system."

Thanks to the integrated SafeChangeFilter technology, Kemper enables a contamination-free filter change. In this way, welders do not come into contact with the harmful hazardous substances in the welding fumes — even during disposal. An integrated lifting device facilitates the filter change. Due to the mechanical operation, the system is energy self-sufficient.

MORE INFO www.kemper.eu

Gasbarre delivers furnace for aerospace manufacturer

Gasbarre Thermal Processing Systems shipped a continuous vacuum furnace with 10 BAR pressure quench capabilities to a major aerospace manufacturer in North America. The four-position, four-zone furnace is rated to 2,400°F. The independent load and quench modules allow the heat module to hold temperature and vacuum, creating an extremely pure environment. Extended heating element coverage allows for excellent temperature uniformity. As only the workload is cooled in the isolated cooling chamber, it makes for an efficient system. Quick transference from the heat module to the cool module and fast quench capabilities make this an ideal vacuum furnace to process medium- to high-volume parts. Gasbarre was chosen as the equipment



Gasbarre Thermal Processing Systems has been designing, manufacturing, and servicing a full line of industrial thermal processing equipment for nearly 50 years. (Courtesy: Gasbarre Thermal Processing Systems)

supplier based on proven performance from past projects with this manufacturer, as well as extremely low down-time metrics with their existing Gasbarre vacuum furnace equipment.

With locations in Plymouth, Michigan; Cranston, Rhode Island; and St. Marys, Pennsyslvania; Gasbarre Thermal Processing Systems has been designing, manufacturing, and servicing a full line of industrial thermal processing equipment for nearly 50 years. Gasbarre's product offering includes batch and continuous thermal processing equipment for both atmosphere and vacuum applications as well as a full line of alloy fabrications, replacement parts, and auxiliary equipment, which consists of atmosphere generators, quench tanks, washers, and charge cars. Gasbarre's equipment is designedby experienced engineers and metallurgists.

MORE INFO www.gasbarre.com

PermaFlex™ ID tag conforms to curved surfaces

PermaFlex™ is the newest metal identification tag to be added to the PermaLabel® family from InfoSight. PermaLabel is the scratch-proof metal tag that's been the standard for durable asset identification.

InfoSight then produced the PermaLabel® VI which added color coding for fast visual asset identification. These metal tags are rigid and do not conform to curved surfaces very well. With PermaFlex, all of the durable properties and resistance of PermaLabel® exist, with the added benefit of a flexible tag that can conform to curved surfaces.

PermaFlex is attached to products with adhesive. Since the tags retain their shape once curved, they work with the adhesive to remain attached. PermaFlex can be attached to curved surfaces as small as a 1-inch radius. Tag sizes are 3 inches (76mm) wide and range from 0.75 inch (19mm) to 6 inches. (152mm) long. PermaFlex can be printed with one of InfoSight's mill duty LabeLase® Laser Metal Tag Printers.

The new PermaFlex™ identification is well suited for high value assets that have curved surfaces. (Courtesy: InfoSight)

InfoSight is committed to providing identification and traceability in the most difficult environments. PermaFlex continues this tradition in offering a tag for curved surfaces.

MORE INFO www.infosight.com

Accuchiller NQ Series chillers with new upgraded features

Thermal Care has updated its Accuchiller NQ series portable and packaged chillers to include a new control system and cabinetry design.

The newly redesigned NQ Series chillers come standard using an advanced PLC control system with ModBus RTU and a 7-inch color touch screen. This robust control system provides premium performance and extensive diagnostic capabilities with a wide range of communication options including Modbus, BACnet, and LonWorks. Screen layouts are improved to simplify finding data in an easy-to-follow format. Pressure sensors are now included as part of the control system package for even more reliable and accurate

Thermal Care Accuchiller NQ 10 ton air-cooled portable chiller. (Courtesy: Thermal Care)

information. The NQ Series control panel cabinetry is also redesigned to include an ergonomic sloped top for easy viewing and access.

Peter Armbruster, director of sales & marketing at Thermal Care, said, "Precise control technology is so important in today's manufacturing world. Our customers asked for an upgrade and we delivered. This simple-to-use controller comes with complete diagnostic information available at the touch of their fingertips. All the information is right there from settings to troubleshooting and trending data. If you include an optional variable speed compressor package, you have a chiller that can pay for itself in energy savings."

Units were scheduled for shipment on September 15, 2020.

NQ Series portable and packaged chillers are available from four to 40 tons in both air-cooled, water-cooled, and remote condenser models for indoor and outdoor applications.

Founded in 1969, Thermal Care is a developer of leading-edge process cooling technology with energy-saving and cost-efficient product designs. The company provides heat transfer equipment to more than 50 industries and specializes in meeting the specific needs of all customers by offering both standard and custom designed industrial process cooling solutions. Thermal Care's broad product line includes portable and central chillers, cooling towers, pump tanks, and temperature controllers. The company also delivers extensive experience and engineering knowledge to develop and execute plant-wide cooling solutions.

MORE INFO www.thermalcare.com

Indian company adds fourth furnace from Seco/Warwick

Harsha Engineers Limited, a leading bearing cage manufacturer in India who has manufacturing facilities in India, China, and Romania, and customers across five continents, ordered yet another ferritic nitrocarburizing furnace with ZeroFlow® technology from Seco/Warwick.

ZeroFlow is a modern, energy-saving, and ecological gas nitriding process. ZeroFlow technology allows for maintaining full versatility of conventional gas nitriding while optimizing process gas consumption, i.e. a significant reduction thereof concerning competitive technologies. Depending on the type of processed details, steel grade, and final requirements, this method allows for saving gas consumption, including ammonia, by up to several dozen percent as compared to traditional methods.

Modern gas nitriding with the use of ZeroFlow technology, using Seco/Warwick products, fits into the current trends and demands of modern industry.

On one hand, it deals with an innovative method of process control that maximizes the use of the factors that influence processing costs. On the other hand, there is modern equipment that improves the economy through the further reduction of energy consumption and cycle times.

Savings, flexibility, precision, and simplicity of the ZeroFlow® process makes it the ideal replacement for traditional nitriding systems.

Modern gas nitriding with the use of ZeroFlow technology, using Seco/Warwick products, fits into the current trends and demands of modern industry. (Courtesy: Seco/Warwick)

The furnace is equipped with a vacuum system, gas control system, turbo cooling, atmosphere cooling system, and post oxidation system to get a material very uniform gray color and other tribological properties to meet the specifications of leading bearing manufacturers.

The nitrogen potential control is based on hydrogen analyzer and allows measurement and regulation of nitrogen atmosphere potential by measuring the hydrogen content in the furnace atmosphere. Also, all the process parameters such as ammonia flow, carbon dioxide flow, a ratio of carbon dioxide to ammonia, and furnace pressure are automatically regulated. The furnace control system employs a cascade-based temperature control system to regulate the furnace temperature very closely to meet the requirements of the customer.

"Our relationships with Harsha are both personal and professional. Information is shared on a top management level as much as on operational levels. Thanks to long term cooperation the communication is close and transparent. Because of all this, we have been supporting our client not only in process optimizations and crew training, but also developed parts at our R&D center, and give regular technological and metallurgical support in improving their product quality," said Manoranjan Patra, managing director of Seco/Warwick India.

"Harsha Engineers is a demanding and technically aware customer who was very actively involved in developing the concept and even designing the device, so these specific furnaces are tailored in a sophisticated way to their needs and expectations. Harsha team are advanced technically and know very well what they want.

"The fact that the client ordered its fourth furnace from Seco/Warwick confirms our strong position in this particular industry," Patra said.

Seco/Warwick has been consistently supplying its best technologies securing for the client repeatable productivity, maximum performance, and strong service support.

"ZeroFlow is an excellent solution to a fast-growing Indian market where companies from different sectors strive to provide an increasingly better quality of processed parts. Seco/Warwick grows into first-choice company position in nitriding technology and a ferritic nitrocarburizing furnace for heat treating bearing at this market," said Sawomir Woniak, CEO at Seco/Warwick.

MORE INFO www.secowarwick.com

Ceramics Expo announces online event for 2020

Ceramics Expo's 2020 installment of America's largest free-to-attend event for the ceramics industry will be hosted online September 21-25.

Ceramics Expo Connect 2020 will bring four days of interactive events, peer-to-peer discussions, networking, and more than 250 industry suppliers to the sector and its supply chain — all accessible from the comfort and safety of peoples' home or office without any travel.

On each day, the conference will focus on a different theme including facilitating a clean, connected and electrified technology, additive manufacturing, aerospace applications, and quality and testing. A series of panel discussions and breakout sessions will cover trends and applications, materials and manufacturing. Industry experts will also weigh in on business continuity and key developments in the market following the global disruption caused by COVID-19.

An online platform has been created by the event organizers, with a user-friendly interface that can be personally customized to ensure that all attendees will get all the benefits of attending the conference in-person. One-to-one meetings with suppliers can be booked in advance and panel debates will be followed by virtual networking. The online conference program features more than 50 people from global companies and academia, including NASA, Ford, DuPont, Moog, and ASTM International, among others.

Danny Scott, event director at Ceramics Expo, said, "We're thrilled with how Ceramics Expo Connect has come together and that the industry can still virtually meet, connect, and explore partnerships and collaborations, despite the restrictions due to COVID-19. Furthermore, the online event has unlocked the potential to reach even more people that will benefit from connecting with the community globally. We're anticipating a diverse range of attendees which will undoubtedly bring something different and innovative to the discourse at this year's event."

Now in its sixth year, Ceramics Expo attracts representatives from the automotive, aerospace, electronics, renewable energy, medical, telecommunications, utilities, energy storage, and defense spaces.

All sessions are free to attend, and visitors can find out more information or register their interest in joining at the website below.

MORE INFO www.ceramicsexpousa.com

Solar Atmospheres builds a future for vacuum oil quenching

The 15,000-square-foot expansion continues at Solar Atmospheres of Western PA. (Courtesy: Solar Atmospheres of Western PA)

The novel coronavirus (COVID-19) pandemic has affected every industry and business globally.

"We have had to think on our feet, find innovative solutions and pivot quickly, to change protocols to protect our employees and to safeguard our business," said Bob Hill, president of SAWPA. "At first, it seemed almost necessary to pause our business, take time to figure out every minute detail to play it safe. However, that philosophy was not how we built this business after the 2001 recession, nor would that have supported our employees, their families and our customers today."

Solar views this period as a way to set new paths of transformation and growth for the company. It has encouraged the adoption of the newest technology, such as vacuum oil quenching (VOQ). The latest VOQ quench line, including a hardening furnace, tempers, washer, and charge car, will be installed and fully operational by the end of 2020. To make room for this innovation, SAWPA continues to progress in the construction of its 15,000-square-foot addition. Solar believes this is a time for all business to look at strategic ventures and new diversified offerings with a new lens to better serve this ever-changing environment.

MORE INFO www.solaratm.com

Accurate Brazing hires Southeast sales manager

Accurate Brazing hired Jennifer McPeek to the newly created position of Southeast regional sales manager. McPeek will focus on sales and marketing for brazing, heat-treating, and HIP'ing customers in Florida, Georgia, and Alabama.

"We are very excited to have Jennifer join Accurate Brazing. She has a proven track record developing customer relationships and generating sales growth. She will be a vital part of Accurate Brazing's sales and marketing strategy and growth into markets for not only our brazing and vacuum heat-treating services, but also our HIP'ing capabilities," said Brent Davis, vice president of Accurate Brazing.

Jennifer McPeek

McPeek joins Accurate Brazing with more than 30 years of experience in the brazing and heat-treat industry, working with customers across the aerospace, automotive, and general industry sectors, and brings with her extensive connections throughout the United States.

Accurate Brazing, a subsidiary of Aalberts n.v., is a full-service, one-stop shop for vacuum brazing, heat-treating, and HIP'ing with more than 30 years in the business, tailored primarily to support the aerospace, additive, and power generation markets. Accurate Brazing has facilities in South Carolina, Connecticut, and New Hampshire.

MORE INFO www.accuratebrazing.com

Pennex Extruded Products names president

Chuck Stout has been promoted to president of Pennex Aluminum Company Extruded

Products Division. In his new role, Stout will be responsible for the overall strategic, financial, commercial, and operational functions for the extruded products businesses in Wellsville and York, Pennsylvania, and Leetonia, Ohio.

A veteran of the U.S. Navy, Stout joined Pennex in 2016 as general manager of the Leetonia, Ohio, location. He has an impressive background in the manufacturing industry including roles as plant manager and vice president of operations. His office will remain in Leetonia.

Stout said, “It is an honor to take the reins of a very successful extrusion business and lead a highly engaged team of people that are extremely committed to serving our customers. They are incredibly proud of their past recognition as tops in the industry in total customer satisfaction and energetically carry on that legacy.”

Chuck Stout

“Chuck adeptly navigated our Ohio location through the $25 million expansion of our advance manufacturing fabrication facility,” said Rick Merluzzi, chief executive officer of Metal Exchange Corporation. “He personifies our core values of safety, integrity, respect, and drive and clearly embraces our ‘dual bottom line’ leadership style, which prioritizes the safety and well-being of employees equal to financial success.”

MORE INFO www.pennexaluminum.com

Dante Solutions’ Dante 5.0 software goes live

Dante Solutions, Inc. has released Dante 5.0, the most advanced heat-treatment simulation software from Dante Solutions. Included in Dante 5.0 are several new features designed to describe the physics of steel heat treatment more accurately; they include:

› **Carbon Separation Model:** This model describes the rejection of carbon as the steel transforms to ferrite from austenite. The additional carbon then enters the surrounding austenite matrix, increasing the local hardenability of the steel.

› **Carbide Decomposition Model:** This model describes the decomposition of primary carbides during heating processes. The decomposition rate is a function of time, temperature, and carbide size factor.

› **Residual Stress Relaxation Model:** This model describes the relaxation of residual stresses during heating and holds at high temperature. The relaxation rate is a function of time, temperature, and stress.

› **Alloy Composition Variation Modeling:** Dante 5.0 introduces the ability to model slight variations in steel alloy composition and its effect on the material’s hardenability.

❯ **Liquidus/Solidus Latent Heat Model:** This model describes the latent heat released as a steel transforms from the liquid state to the solid state and the latent heat absorbed as a steel transforms from the solid state to the liquid state.

❯ **Abaqus Plug-In:** Dante Solutions has developed an Abaqus Plug-In designed to aid in Dante model setup. The Plug-In includes means to define material, initial conditions, boundary conditions, and more.

❯ **Dante Utility GUIs:** Dante Solutions has developed Graphical User Interfaces (GUIs) for all of its utilities offered to aid in material, model, and process development.

❯ **MatSim Utility:** Dante Solutions' latest utility combines the power of the Dante phase transformation models into an easy-to-use utility.

MORE INFO www.dante-solutions.com

Trends, information, and technology for precision cleaning

In times of contact restrictions, travel constraints, and trade show cancellations, the virtual customer day scheduled by the Swiss company UCM AG offers customers and interested parties a safe way of keeping up to date with the latest developments in the field of precision and ultrafine cleaning. Presentations in German and English will inform about current trends and demands, as well as about solutions and innovative processes for meeting the requirements set by many industries for ever-cleaner parts. The innovative UCMSmartLine will also be showcased for the first time at the digital exhibition booth on September 29, 2020.

Companies from sectors such as the medical engineering, optics, automotive and supplier industries, precision engineering and microtechnology, and high-purity processing are confronted with ever-increasing cleanliness requirements related to particulate and film-type/chemical contamination. Solutions are often discussed at a trade show, but since that is not possible this year, the Swiss company UCM AG — a division of the SBS Ecoclean Group specializing in precision and ultrafine cleaning — is staging a digital customer day with a virtual exhibition booth.

One of the highlights of the online event will be the first-time presentation of the novel smart solution for efficient precision and fine cleaning, UCMSmartLine. The innovative and cost-efficient ultrasonic cleaning series is based on standardized modules, including not only integrated electrical and control technologies for the process steps of cleaning, rinsing, drying, loading, and unloading but also a versatile transport system. The customer day is free of charge. The virtual exhibition booth can still be visited after the online event.

MORE INFO www.ucm-ag.com
www.ecoclean-group.net

INDUSTRIAL HEATING EQUIPMENT ASSOCIATION

Check out IHEA webinars, online education

IHEA strives to provide a base of industry knowledge for our members and users in the industrial process heating industry. Many valuable resources can be found on the IHEA website, www.ihea.org. Click on the Education & Events tab to find information on all our educational materials, training courses, and technical information available.

IHEA LEARNING ACADEMY

This is the place to access online training videos on process heating industry technologies. You will find a variety of educational presentations designed to provide an understanding of many industrial process heating technologies. Check back often for additions to the video library.

BOOKS

IHEA's online bookstore offers a range of titles for purchase including the recently revised third edition of the Infrared Process Heating Handbook.

WEBINARS

IHEA's archived webinars are available at no charge. View them on your own time.

› **Fundamentals of Combustion:** This webinar explores the fundamental combustion topics of combustion triangle, air-to-fuel ration, heating value, and combustion efficiency.

› **The Ins and Outs of Infrared:** Three IHEA members present the basics of infrared technology and its widespread applications.

› **Basics and Applications of Induction:** Learn about the basics of induction technology and how the electrically powered induction technology can create heat-in parts, up to and including melting metals.

WHAT IHEA MEMBERS SAY ABOUT THE BENEFITS OF IHEA'S EDUCATIONAL PROGRAMS:

"Many of our engineering positions have a requirement to be trained in IHEA's NFPA86 and Fundamentals of Industrial Heating courses. We think IHEA's courses are a great way to get them started in their positions.

— *Albert Cantu, Nutec Bickley*

"IHEA offers many benefits for Super Systems Inc. Because of the member discount, we have sent our engineers to the training seminars. They bring back great knowledge and make connections during the class."

— *Bob Fincken, Super Systems Inc. (SSi)*

IHEA members benefit from reduced registration fees for courses and seminars as well as a discount in the IHEA bookstore. For more information on becoming an IHEA member, go to www.ihea.org/page/benefits

STILL TIME TO REGISTER

Fundamentals of Industrial Process Heating Online Course

October 5-November 15, 2020

IHEA's Fundamentals of Industrial Process Heating Online Learning Course continues to provide a high level of learning to those in the industrial heat processing industry. Scheduled to begin October 5, the six-week class will run through November 15. The flexible online format and interactive forums with other students, along with scheduled office hours with the instructor are just a few of the benefits of this program. Weekly coursework, quizzes, and a final exam project are administered to guide students on their progress and evaluate their knowledge of the material. For a complete listing of the topics covered, got to www.ihea.org/event/FundamentalsFall20

Registration fee includes an electronic course handbook, course instruction, quizzes and projects, class forums, and the opportunity to contact the instructor throughout the course. Printed materials are available for an additional fee. IHEA members receive a registration discount, and there is also a registration discount available for two or more registrants from the same company.

Register now: www.ihea.org/event/FundamentalsFall20

IHEA 2020 CALENDAR OF EVENTS

OCTOBER 5–NOVEMBER 15

Fundamentals of Process Heating On-Line Course

6 Week Online Course | Registration open until October 1

This course provides an overview of the fundamentals of heat transfer, fuels and combustion, energy use, furnace design, refractories, automatic control, and atmospheres as applied to industrial process heating. Students will gain a basic understanding of heat transfer principles, fuels and combustion equipment, electric heating and instrumentation and control for efficient operation of furnaces and ovens in process heating.

OCTOBER 20–21

Powder Coating & Curing Processes Seminar

Alabama Power Technology Applications Center | Calera, Alabama

The day and a half Introduction to Powder Coating & Curing Processes Seminar will include classroom instruction and hands-on lab demonstrations.

For details on IHEA events, go to www.ihea.org/events

INDUSTRIAL HEATING EQUIPMENT ASSOCIATION

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D. SCOTT MACKENZIE, PH.D., FASM
SENIOR RESEARCH SCIENTIST–METALLURGY /// QUAKER HOUGHTON INC.

When quenching aluminum, it is crucial to maintain the supersaturated solid solution down to room temperature by using rapid quenching.

Heat treatment of aluminum – Part I: Quenching basics

In previous articles, we discussed the role of alloying elements and discussed the solution heat treatment of aluminum. We showed that it is important for all the alloying elements to be in solid solution prior to quenching.

In this article, we will show the most critical aspects of quenching aluminum. In many respects, this is the most critical operation in the entire process of heat-treating aluminum.

The fastest quenching rate will achieve the best combination of strength and toughness.

QUENCHING

The fundamental objective of quenching is to preserve, as nearly as possible, a solid solution formed at the solution heat-treating temperature by rapidly cooling to room temperature. This maintains the solute in a super-saturated solid solution and maintaining an adequate supply of vacancies required for subsequent precipitation. When quenching rates from the solution temperature are not sufficiently rapid to retain the solute in solution or maintain adequate vacancy concentration, the solute will precipitate on grain boundaries, or dispersoids. Vacancies migrate very rapidly to disordered regions like grain boundaries. The amount of precipitation occurring during quenching reduces the amount of subsequent hardening possible. This is because as solute is precipitated from solution during quenching, it is unavailable for any further precipitation reactions. This results in lower tensile strength, yield strength, ductility, and fracture toughness.

The fastest quenching rate will achieve the best combination of strength and toughness. Resistance to general corrosion and stress-corrosion cracking is also improved with maximum quenching rates. The preferential formation of precipitated phases at grain boundaries during quenching or subsequent artificial aging also is extremely important in relation to corrosion resistance and stress corrosion cracking. Grain boundary precipitation is frequently accompanied by development of thin layers of precipitate-free zones adjacent to the boundaries. (Figure 1) Resistance to corrosion and to stress-corrosion cracking are generally improved by maximum rapidity of quenching, although some of the alloys used in artificially aged tempers are exceptions to this rule. For example, the resistance to corrosion of aluminum-copper alloys in the artificially aged condition is less dependent on a rapid quench than when in the naturally aged temper.

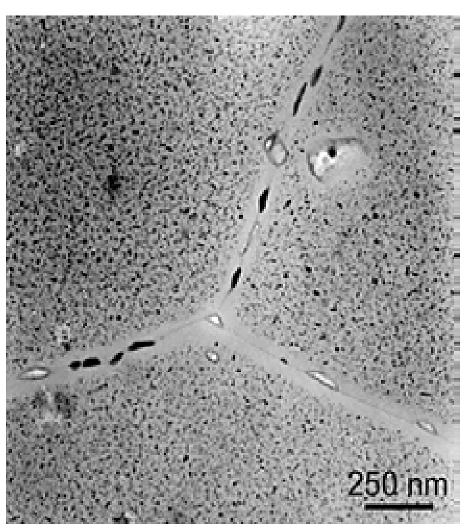

Figure 1: Grain boundary precipitates and precipitate free zones (PFZ) in a 7050 alloy as the result of slow cooling during quenching [1].

A maximum cooling rate is not the only thing that must be considered. Residual stresses and distortion increase with increasing quench rates. A balance between the maximum quench rate and distortion must be maintained. In general, this means that the fast quench rate that just satisfies the desired properties should be used.

The quench sensitivity of the alloy means that some alloys are less sensitive to quench rate than others. For example, an extended delay in quenching generally results in lower mechanical properties of a quench-sensitive alloy such as 7075. Other alloys, such as 2024, are less sensitive to the effect of quench rate on mechanical properties but can be affected adversely by lowered resistance to corrosion as the quench rate is reduced. It has been found that in the case of 7XXX alloys [1] that quench rates greater than 100°C/sec offer no additional benefit to strengthening, but can drastically contribute to increased residual stresses and warpage.

The kinetics of precipitation occurring during quenching is dependent on the degree of solute supersaturation and the diffusion rate as a function of temperature. So, as an alloy is quenched, there is greater supersaturation (assuming no solute precipitates). But the diffusion rate increases as a

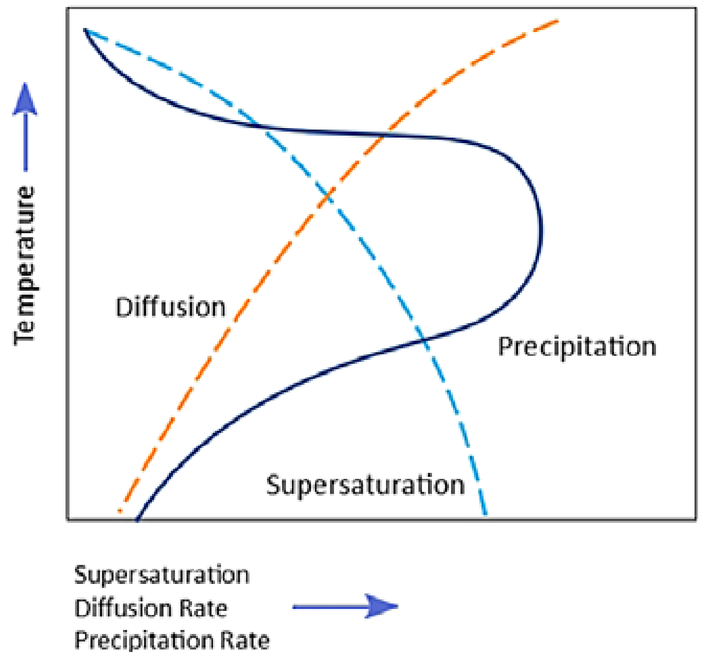

Figure 2: Schematic representation of the effect of temperature on diffusion, supersaturation, and precipitation [2].

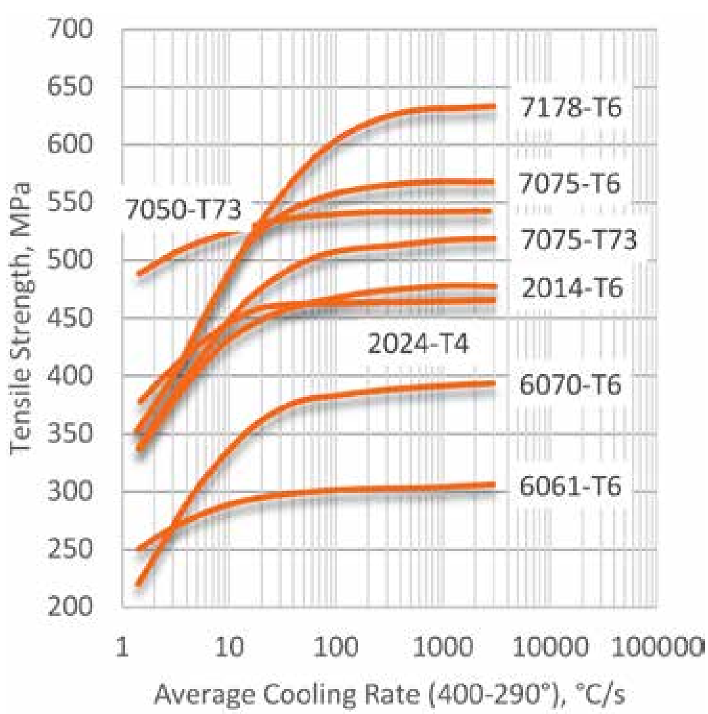

Figure 3: Tensile strengths of eight alloys as a function of average cooling rate during quenching [2].

function of temperature. The diffusion rate is greatest at elevated temperature. When either the supersaturation or the diffusion rate is low, the precipitation rate is low. At intermediate temperatures, the amount of supersaturation is relatively high, as is the diffusion rate. Therefore, the heterogeneous precipitation rate is the greatest at intermediate temperatures (Figure 2).

For most aluminum alloys, the critical temperature range is 400°C – 300°C. This means that quenching must occur rapidly through this range to prevent solute precipitation.

Quantifying quenching, and the cooling effect of quenchants, has been extensively studied [3] [4] [5] [6] [7]. The first systematic attempt to correlate properties to the quench rate in AlZnMgCu alloys was performed by Fink and Wiley [8] for thin (1.6 mm) sheet. An illustration of the effect of average cooling rate from the solution heat-treating temperature on tensile strength is shown in Figure 3. As can be seen, there appears to be a maximum average quenching rate of approximately 100°C/sec where little additional benefit from increased quenching rate is observed.

Average quench rates are useful in comparing experimental results from various quench methods. However, average quench rates only compare results in a "critical" temperature range, where precipitation is most likely to occur. This method is not entirely accurate, because significant precipitation can also occur outside the specified critical temperature range of average quench rates. Moreover, for high-strength alloys, toughness and corrosion resistance may be impaired without significant loss of tensile strength.

For most specifications used for aluminum heat treating, the delay time is measured from the time the furnace door is first opened, or the first portion of the load emerges from the salt bath, or the heating zone of a continuous, to the complete immersion of the load in the quenchant. The minimum thickness used to determine the allowable quench delay is the minimum dimension of the thinnest section of the load.

The specification of a maximum quench delay prevents the solution heat-treated load from cooling excessively during transfer to the quench tank. It ensures that the maximum properties are achieved. Exceeding the maximum allowable quench delay can result in a "slack quench," and excessive precipitation of the solute on grain boundaries or other sites, preventing participation in subsequent aging.

CONCLUSIONS

In this short article, we discussed the basic metallurgy behind quenching aluminum. It is necessary to maintain the supersaturated solid solution down to room temperature. This is achieved by rapid quenching. In the next article, I will discuss quenchants for aluminum.

As always, should you have any questions or comments regarding this article, or have any suggestions for further articles, please contact the editor or the author.

REFERENCES

[1] D. S. MacKenzie, Quench Rate and Aging Effects in Al-Zn-Mg-Cu Aluminum Alloys, Rolla, MO: University of Missouri - Rolla, 2000.

[2] J. E. Hatch, Aluminum: Properties and Physical Metallurgy, Metals Park, OH: American Society for Metals, 1984.

[3] M. A. Grossman, Metals Progress, vol. 4, p. 373, 1938.

[4] H. Scott, "Quenching Mediums," in Metals Handbook, Cleveland, ASM, 1948, p. 615.

[5] F. Wever, Archiv fur Eisenhuttenwesen, vol. 5, p. 367, 1936.

[6] L. Dakins, Union Carbide.

[7] B. Liscic, H. M. Tensi, L. C. Canale and G. E. Totten, Eds., Quenching Theory and Technology, Boca Raton, FL: CRC Press, 2010.

[8] W. L. Fink and L. A. Wiley, "Quenching of 75S Aluminum Alloy," Trans. AIME, vol. 175, p. 414, 1948.

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TONY TENAGLIER
HEAT TREAT PROCESS ENGINEER ///
HITCHINER MANUFACTURING

Pyrometry is a requirement that is intimidating, but, at the same time, it brings clarity and control to a heat-treat process.

AMS2750 pyrometry revisions tweak a crucial process

AMS2750 pyrometry is a daunting heat-treat special process requirement in the aerospace industry. It's a literal definition implying measurement of temperature, but it also defines a measurement system of extreme detail and consistency for a given heat-treat process. It is a specification that brings clarity to a process of bringing control to heat-treat, but also one that creates a headache if the parameters are not fully understood — not only from the technical requirements, but from a realization as to why these requirements are necessary.

The instruments on a furnace take the signals from the sensors and convert the mV signals to degrees. AMS2750 requires specific instrumentation types to be defined and including how many and what types of instruments are needed to convert these signals on various parts of the furnace.

THE SCOPE OF THE SPECIFICATION

By definition, "This specification covers pyrometric requirements for equipment used for the thermal processing of metallic materials. Specifically, it covers temperature sensors, instrumentation, thermal processing equipment, correction factors and instrument offsets, system accuracy tests, and temperature uniformity surveys. These are necessary to ensure that parts or raw materials are heat-treated in accordance with the applicable specification(s)."

THE BREAKDOWN

Sensors equal the eyes into the furnace. The Seebeck Effect describes when two dissimilar metals join together, it creates differences in electrical conductivity. This phenomenon creates the eyes into the furnace — the vision required to see the heat and the heating of the parts. There are three ways to heat something: via conductance, convection, and radiation. A thermocouple is a sensor that measures temperature. It consists of two different types of metals, joined together at one end.

As long as the tip of the thermocouple is the only junction along the length of the wire and it is placed in the correct location, it will "see" the particular method of heating.

Thermocouples can come in different types, such as noble and base-metal categories of materials and are further categorized by sheath considerations such as expendable (e.g. woven fabric) and non-expendable (e.g. metal sheath). A thermocouple is often designed and rated for specific temperature ranges, atmospheres in the furnace, and number of uses. AMS2750 lays this out in the respective tables by establishing recalibration and use frequencies based upon a temperature.

However, mV differences do not mean much from a heat-treat perspective, and these values need to be converted into a value of more meaning to be understood.

CALIBRATING

Instrumentation calibrations equal converting what the sensors see to something to which one of our human senses can relate. The instruments on a furnace take the signals from the sensors and convert the mV signals to degrees. This is the constant work that goes on during the entire process of controlling and recording the temperature cycle. Because of that, it becomes important to check the instruments of controlling and recording on a set frequency to make sure they are doing what they are supposed to be doing. AMS2750 requires specific instrumentation types to be defined and including how many and what types of instruments are needed to convert these signals on various parts of the furnace. Often, a customer will require a minimum instrumentation type to be followed. A common instrumentation type for a furnace is Type B.

Type B requires for actual instruments, an overtemp, controller, and recorder. For a Class 3 instrumentation Type B furnace, it is required to check these instruments on a quarterly basis with an accuracy of ±2°F or 0.2 percent, whichever is greater. (Although some customers might have a tighter accuracy requirement.)

One might think from the metallurgist's perspective that this degree of accuracy seems insignificant on the microstructure if the temperature is 2,000°F or really 2,001°F and to further require the use of correction factors of the thermocouples that can vary 10ths of degrees to get a true reading of now 2,000.5°F, for example. This accuracy of temperature seems irrelevant when considering the activa-

tion energy required for the atom to diffuse into a vacant lattice site.

Often the heat-treat temperatures established for the process are not on the cusp of the potential energy required to move the atom, but in a range where it seems almost guaranteed. However, as an archer aims specifically at the bullseye to hit the target with an arrow, the focus in heat treat must be to an extreme point. This allows for the slightest miscue, while often still resulting in hitting the desired target.

SYSTEM ACCURACY TEST (SAT)

Ideally, an SAT is used to make sure the system of sensor plus the lead wire plus the instrument all work. The system accuracy test, so nicely described in Revision F in comparison to Revision E, lays out three methods: comparison, alternate, and the waiver. This begins to test the overall function of the system when the elements are combined — how the eyes work in conjunction with the brain of the furnace. The components themselves can be working, but the overall combination of these components must work in unison. This test, although simple in nature, is often required by an auditor to witness during the Nadcap audit.

IN THE ZONE

The Temperature Uniformity Survey (TUS) means defining the work zone and understanding the temperature variation in the furnace (defining the space of the furnace to be the working zone and determining the uniformity in each region of the furnace). It is the volume in which to guarantee the parts heat treat correctly and where the spatial recognition for the eyes of the furnace is monitored during a heat-treat cycle. This is a test that exposes the integrity of the furnace. Any wear-and-tear on the hot zone itself will result in temperature variations that exceed requirements. It's a test of the heating components — such as graphite elements — in a vacuum furnace that is working correctly with no electrical shorts or inconsistent radiation.

The TUS really begins with the furnace design and the manufacturer's responsibility to adequately design and control the heat the best way possible. It then requires the patience of the engineer to adjust the power to the zones and to trim the furnace parameters into tolerance.

CONCLUSION

Pyrometry is a requirement that can be intimidating, but, at the same time, it can bring clarity and control of a process. Beyond the specific technical requirements, it symbolizes steps to follow to ensure repeatability and confidence for a given heat-treat cycle. There is little room for error when flying a plane; similarly, on the ground, there should be no relaxation of the strict expectations of demanding a sound process that is in control to be as specific as possible. And to prove that quality counts, AMS2750 requires quality assurance personnel to sign off on the pyrometry records.

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ADVANTAGES OF WIRE-ARC ADDITIVE MANUFACTURING

3D Printed Tooling, Vallourec. (Courtesy: Lincoln Electric)

3D printing technology has historically been restricted to printing small components, but Lincoln Electric's wire-arc AM is breaking size and weight barriers with its innovative process.

By KENNETH CARTER, Thermal Processing editor

The concept of additive manufacturing has been around for a century, but with the advent of sophisticated software and robotics, the process is fast becoming a game changer in the manufacturing world.

3D printing — a term often used interchangeably with additive manufacturing — has been used successfully to manufacture small components, but when it comes to creating larger, stronger parts, the technology has been relatively limited.

But wire-arc additive manufacturing is expanding 3D printing, and it is proving to be extremely innovative in a way that makes it possible to create big, heavy parts for industries such as aerospace, construction equipment, transportation, and more.

"We certainly see any heavy industry as a great opportunity," said Mark Douglass, Ph.D., CFA, business development manager for Lincoln Electric Additive Solutions. "Heavy industry could be steel or metals manufacturing to mining, construction, and farm equipment. It could include the energy markets such as oil and gas and power generation (e.g. natural gas, nuclear, and hydro), as well as transportation like larger trucks and ships, whether commercial ships or defense. And with aerospace, it's really interesting seeing 3D printing being used by the space guys. They're very interested in this, whether it's for satellites or rocket launches."

WHAT IS WIRE-ARC AM?

With a plethora of industries excited about what wire-arc additive manufacturing can do for them, what exactly is it about this technology that is pushing it to the top of everyone's wish list?

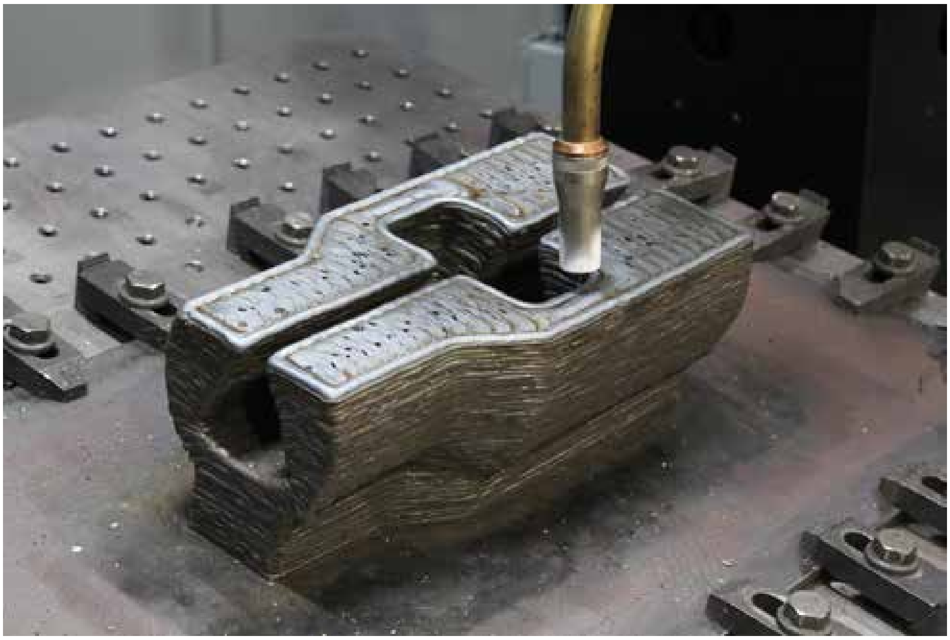
Wire-arc additive manufacturing often employs the process of gas metal arc welding (GMAW). This is also known as MIG welding. The arc welding power source generates electricity to create an arc between a wire feed stock — usually some type of steel or metal alloy — and a substrate. The arc generates heat sufficient to melt the wire onto the substrate.

With GMAW as the base process to melt the wire, an automation system is needed to deposit the material accurately and repeatedly. Sophisticated software slices a solid CAD model into layers and then programs the machine with the optimal path in which to deposit the feed stock material.

"Think about laying down a series of welds next to each other to create a layer, and then stacking another layer on top of that; there are any number of ways you can do that," Douglass said. "For example, printing a basic square one could start on the outside of the perimeter of the square and then just keep going further in a spiral type motion. Or you could start in, and then spiral out. You could start on one side and zigzag back and forth. Instead of going North/South, you could go East/West, or you could do a 45-degree pattern."

Douglass compares it to the tool path on a CNC cutting router.

"Similar to CNC machining, there are a variety of ways to generate the tool path and decide how you're going to machine a part," he said. "And based on experience, a machinist or programmer will understand how best to cut a part. Ours is similar, except we're automating that process. It's not something that is manually created."



A functional prototype of an oil-and-gas valve housing. (Courtesy: Lincoln Electric)

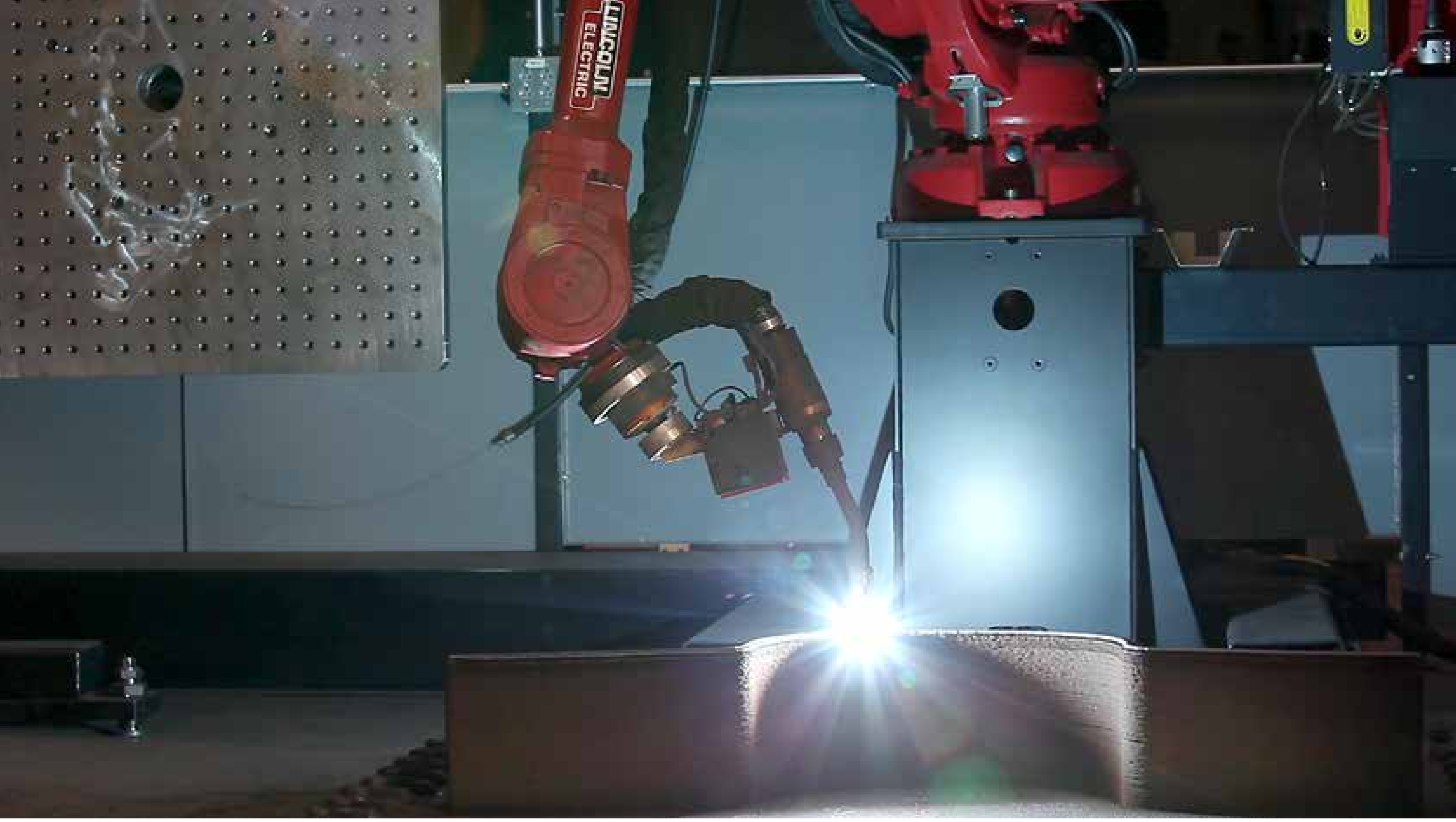
GOING BIG

But while previous 3D-printing methods only have been focused on creating small parts from plastic and metals, the wire-arc additive manufacturing process has the ability to create large, metal parts.

"We're using robotic systems, which provide a large degree of flexibility," Douglass said. "Our current systems are able to print parts roughly 4 feet by 6 feet by 6 feet tall, but the theoretical part size is unlimited for wire-arc additive. We've printed parts over 1,500 pounds but can go much larger."

The process is ideal for manufacturing large-scale or large-format parts quickly as compared with other additive manufacturing methods, such as powder bed or binder jet.

"Metal wire is less expensive, simpler to utilize, and safer than powder," Douglass said. "And, importantly, the rate at which you can melt the wire and deposit the material is an order of magnitude higher than powder."



Lincoln Electric Additive Solutions 3D prints large-scale metal parts. (Courtesy: Lincoln Electric)

The deposition rate is often given as pounds-per-hour. By using wire arc, the deposition rate generally ranges from a few pounds per hour to more than 10 pounds per hour for steel.

"With wire arc, you can deposit material quickly, and that's why it's good for large parts because you don't want to spend a month and a half in a really large powder bed machine to make a part," Douglass said.

AEROSPACE APPLICATIONS

Douglass said the technology is being put to good use in the aerospace industry by printing tooling used to make components. A lot of carbon-fiber parts for aerospace applications are manufactured using molds called lay-up molds. The carbon fiber conforms to the mold by holding it down with a vacuum bag that holds the shape of the tool. It's then put in an autoclave in order to cure the final part.

The experts at Lincoln Electric have manufactured lay-up tools out of steel as well as invar, which is a high nickel-iron alloy that is stable across a wide range of temperatures. Being able to use a lay-up mold made from invar gives it the advantage of keeping expansion to a minimum during the curing process.

And since the wire-arc AM systems are open atmosphere, there's no need for a gas chamber where argon or other industrial gases are required. For example, it is possible to create multi-material parts where the robot is equipped with two wire delivery heads with two different types of wire. In the middle of printing, the materials can be switched with practically no time lost in production. This process would allow the core of a hot stamping die, for example, to be made of a high-strength steel that's strong and tough but not hard. Then, the shell of the die can be printed from an extremely hard material that could take the abuse of a stamping operation.

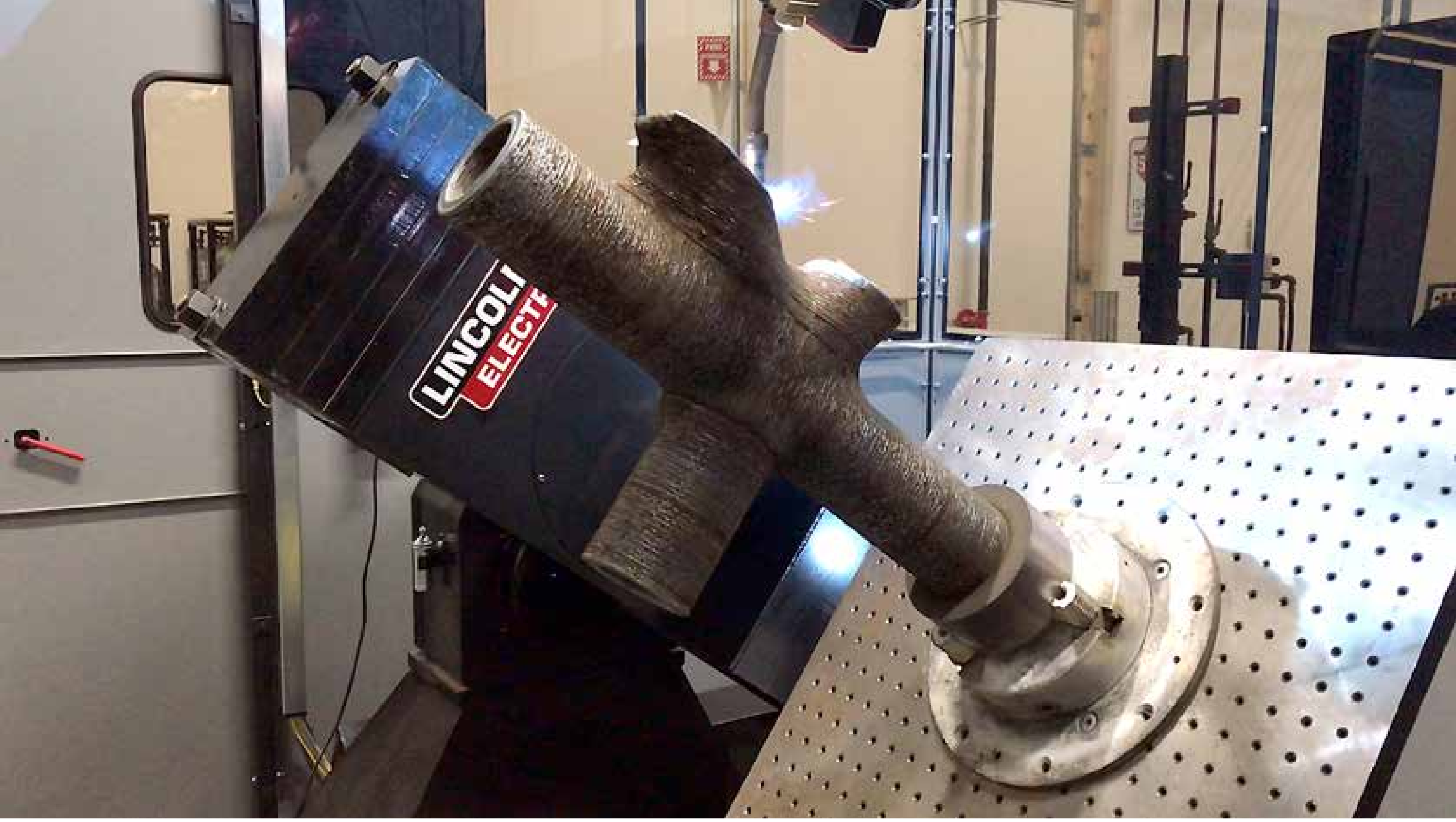
"And the sky's the limit," Douglass said. "You can print more materials than that. And it's really a form of cladding, which has been around for a very long time. Usually cladding is relatively two dimensional, for example cladding a deposit on a pipe. It's one layer, maybe two, but pretty simple; you just spiral around the pipe. With additive technology using coordinated, multi-axis motion between robots and positioners, you can create that deposit in any number of regions and on more complex shapes."

3D-printed and machined invar lay-up mold for aerospace composite manufacturing. (Courtesy: Lincoln Electric)

PRINTING HOLLOW PARTS

With that in mind, the wire-arc AM process can be used to create parts that are hollow or with a structured interior. This allows parts to be not just lighter in weight, but more economical.

There are many components that are designed with the manufacturing process in mind, but generally, manufacturing processes introduce design limitations. For example, machined or cast parts cannot be manufactured with hollow interiors, according to



Lincoln Electric Additive Solutions' technology can 3D-print complex shapes without support structures. (Courtesy: Lincoln Electric)

The wire-arc AM process can be used to create parts that are hollow or with a structured interior. This allows parts to be not just lighter in weight, but more economical. For example, machined or cast parts cannot be manufactured with hollow interiors.

Douglass. However, when designing for additive, engineers have design flexibility to create hollow parts.

"We did that recently for a customer," he said. "It was a prototype mechanical-arm type device. It was about four feet tall, and we hollowed out the inside. We saved 25 percent of the weight, and the additive part performs as well as the standard cast part. In addition, we printed the prototype in less than a week, whereas a casting could take a couple months."

PROTOTYPING ADVANTAGES

Prototyping large parts in a fraction of the time it would take with previous methods is certainly a huge advantage, because, until now with wire-arc AM, rapid prototyping metal parts hasn't been a viable option with components more than a few feet in size.

"We cannot only print you a part that's five, six feet long, but we can print you a functional prototype," Douglass said. "You could actually use it in your application and test the design. Oftentimes, rapid prototyping meant 3D printing plastic parts, and it's really just to help the design engineer understand how the design is going to work, and how the manufacturing engineers are going to assemble the parts. Now, you can do it in metal as opposed to waiting for a casting."

Another advantage is that, once a part has been created, the system settings are on file to print the part again, creating what Douglass calls a "digital inventory."

"In theory, as soon as an order is placed, we can start printing," he said. "It's good for replacement spare parts."

OWNING A SYSTEM

If there is a downside to the wire-arc additive manufacturing, it's that it requires significant resources to maintain a system onsite. To do it properly would involve an investment that could approach $1 million, according to Douglass. And then it would need to be staffed with engineers.

"These systems are not your average manufacturing piece of equipment that an operator can manage," he said. "And that's where we come in. That's where we decided to print parts for customers. I think most customers view it not only as a big, upfront investment, but there is also a steep learning curve to printing parts with quality and efficiency."

That's why it made sense for Lincoln Electric to offer part printing services to its customers.

"That's our business: to take our expertise in the software, automation, welding, and materials, to produce high-quality parts, and give you a rapid turnaround," Douglass said.

MORE INFO additive.lincolnelectric.com

DOES NITRIDING IMPROVE THE CORROSION AND WEAR PROPERTIES OF ADDITIVE MANUFACTURED STAINLESS STEEL?

With the advent of AM, it is important that materials are equivalent to conventional methods of production as the final product still needs to be compatible with a heat-transfer fluid in plants where they are used as a heat-transfer medium. This article discusses recent research relating to low-temperature nitriding in an attempt to achieve even better surface properties for AM stainless steel.

By CHRIS WRIGHT

Many industrial processes require a stable heat source to generate end-products. Heat transfer fluids (HTFs) are commonly used in such processes as heat carriers and a number of options are available to producers, such as steam and mineral-based fluids like Globaltherm M. Historically, steam had been used as a HTF in the 1900s as the primary means of keeping materials viscous enough — like petroleum residues and waxes — so they would flow, and this permitted them to be used in petroleum and chemical processing industries. The need for higher temperatures saw the introduction of mineral fluids as they could be used up to 316°C (600°F) [1]. However, the upper temperature is only one characteristic of a fluid, and the lower temperature and ability to control the fluid at a temperature across its operating range also need to be considered [1]. As an example, Globaltherm M has an operating temperature from minus-10°C (14°F) to 320°C (608°F), and so it has a wider temperature range than steam and pumpability at below zero temperatures (to a minimum value of minus-10°C [14°F]), which can be beneficial and advantageous in certain industrial processes.

Another important aspect when using a heat-transfer fluid is its compatibility with the system it will be used in. Indeed, like an HTF, the construction materials used in a system need to be stable under high and low temperatures and be resistant to corrosion. They also need to demonstrate these properties when filled with an HTF. Most fluids will be non-corrosive to the common metals and alloy used in a system. Austenitic stainless steels are commonly used in industry because of their resistance to wear and corrosion. With the advent of additive manufacturing (AM), it is important that materials are equivalent to conventional methods of production as the final AM stainless steel product will still need to be compatible with an HTF in plants where they are used as a heat-transfer medium.

AUSTENITIC STAINLESS STEEL

There are 57 separate and distinct commercial compositions designated by American Iron and Steel Institute as standard types [2] and are austenitic stainless steels, those that contain chromium-nickel-manganese and chromium-nickel compositions, e.g. 304, 304L (denoting a low carbon version), 309S, 310S (denoting silicon version, 316, 316, 316L, 317, 317L), and are commonly used in chemical, food, medical, and other industries for a wider variety of reasons (See Figure 1) including the fact that they are known for their resistance to corrosion. The relatively poor mechanical properties and wear resistance of these steels restrict their widespread usage, so they are especially interesting from a surface-hardening perspective.

There is a range of austenitic stainless steels that are considered general-purpose stainless steels. However, there are numerous variants within this group with clear benefits to industrial applications. For example, AISI 316L, produced using conventional manufacturing techniques such as casting, has a high molybdenum content and provides improved resistance, compared with other stainless steels such as AISI 304, to chemical agents that cause pitting corrosion (i.e. chlorides, photographic solutions, sulfite liquors, and hypochlorites) [2]. Shell-and-tube heat exchangers have long been constructed from stainless steel. In certain types of shell-and-tubing heat exchangers, AISI 316L is used. This has the advantage of a reduced-carbon content vs. AISI 304, and so minimizes carbide precipitation in the weld zone [2]. In addition to these benefits, there are some downsides, such as its relatively high machining costs, time consuming fabrication, and usage in complex structures that makes it an interesting target for additive manufacturing.

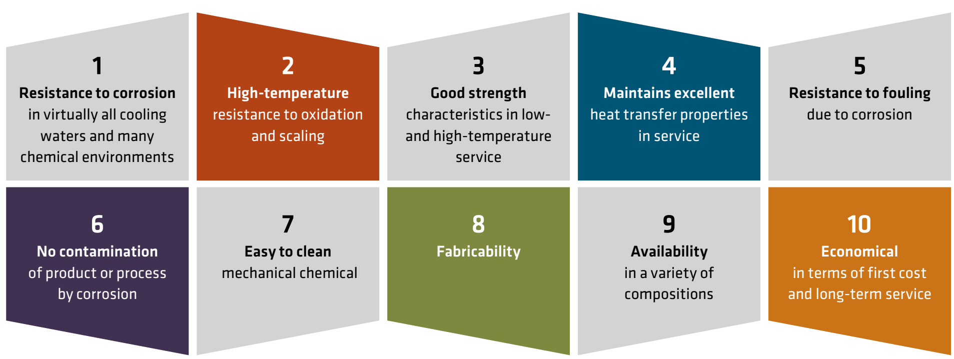
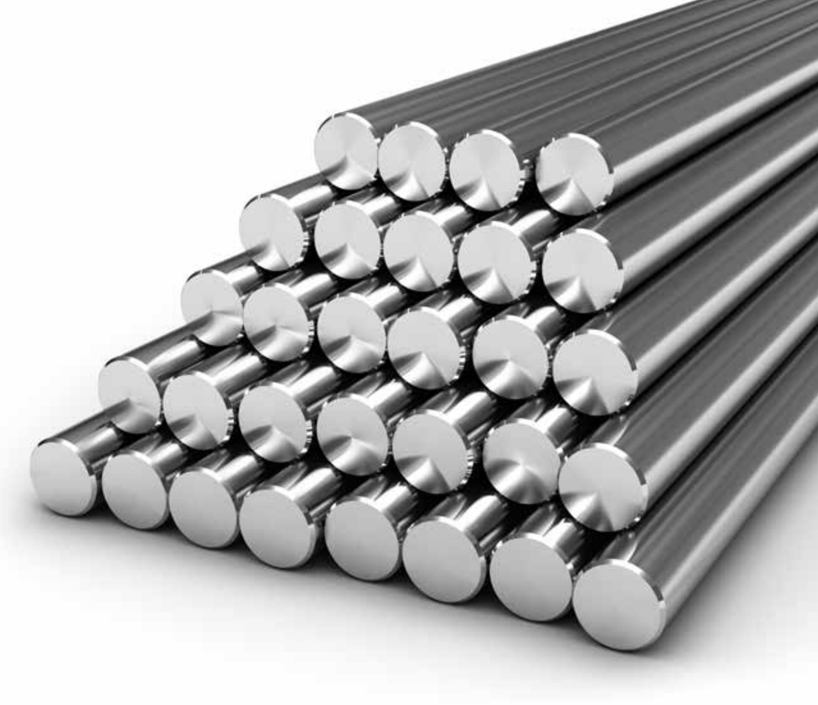


Figure 1: Ten good reasons for using stainless steels in heat exchange equipment [2].

ADDITIVE MANUFACTURING OF 316L STAINLESS STEEL

The AM technique effectively involves layer-by-layer formation using powder or wire as a feedstock and a laser or electron beam to create heat [3]. Much of the research to date has focused on the positive effects of heat-treatment on the wear and corrosion resistance of AM manufactured 316L with the intention of improving material properties to values equivalent to conventionally fabricated AISI 316L.

One of the key challenges to the AM technique is that it leads to residual stresses that decrease the mechanical properties of the stainless steel. These also have a knock-on effect as they affect the dimension of the stainless steel. However, this needs to be weighed against the potential for lower cost manufacturing and improved manufacturing flexibility (from both location and finished product).



PLASMA (ION) NITRIDING

This is a post-manufacturing technique and one approach to hardening the surface of stainless steel, and so it is potentially of interest to AM stainless steels. Nitriding is used to harden a surface and does so by forming two layers on the surface of the steel: the compound layer and the diffusion zone. The outer compound layer is composed of iron nitrides ε and/or γ′ and is formed at the steel surface. The deep and thicker diffusion zone extends into the ferrite matrix where nitrogen is dissolved interstitially and this layer dictates the strength of the hardened surface. Recent research has focused on the post-treating AM 316L using low-temperature nitriding in an attempt to achieve even better surface properties for the treated surface.

ADDITIVE MANUFACTURED 316L AND POST-TREATED, LOW TEMPERATURE PLASMA NITRIDING

Recently, Godec and colleagues [4] conducted a comparative study to assess the effect of nitriding on the hardness, wear, and corrosion resistance of AISI 316L and AM 316L.

Hardness testing results

The nitride layer on the top of the material consists of the S phase and was estimated to be between 13 and 16 μm thick. The Vickers microhardness test revealed that the nitride layer of the AM 316L +nitriding (N) was harder than AISI 316L (1454 vs. 1194 at time zero, respectively) (See Figure 2). It also shows a clear reduction at the border and below the border of the nitride layer. At deeper levels (i.e., 50 to 250 μm in Figure 2), the hardness of the bulk material can be determined and reveals the bulk hardness of AM 316L is higher (i.e. 260 HV0.01 at a depth of 100 μm [the estimated depth of the diffusion layer]) than AISI 316L (200 HV0.01 at the same depth).

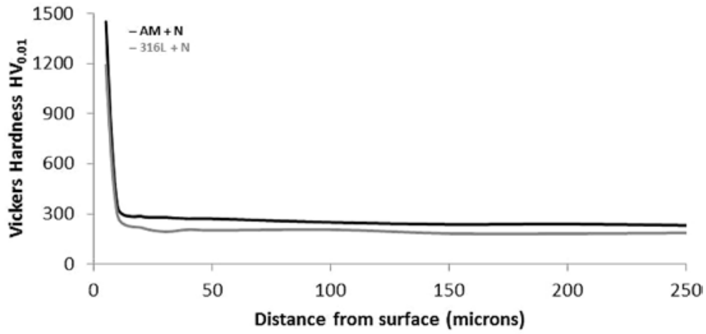


Figure 2: Microhardness HV0.01 depth profile for nitride AM and 316L stainless steel samples. Adapted from [4]: The nitride layer is a 3 to 4 μm layer on the top surface.

Wear-testing results

The test used was a sliding-wear test using a dry-sliding ball-on-flat-surface configuration. The ball measures 32 mm in diameter and is made from 100Cr6 steel. It tests adhesive and abrasive wear from measurements of wear volume and calculations of the steady-state coefficient of friction. Figure 3 shows the overall wear resistance was worse for AM 316L than AISI 316L with higher wear volume and friction. It is also clear that nitriding improves the wear resistance by decreasing friction and largely reducing the volume of lost during testing. After nitriding, the wear benefits improved, but treatment still favored AISI 316L. From these tests, the authors mentioned that, "The differences in the wear volumes of all the nitrided samples show that the nitride layer on the AM sample is slightly less wear resistant, most probably due to the high density of dislocations remaining after the nitriding."

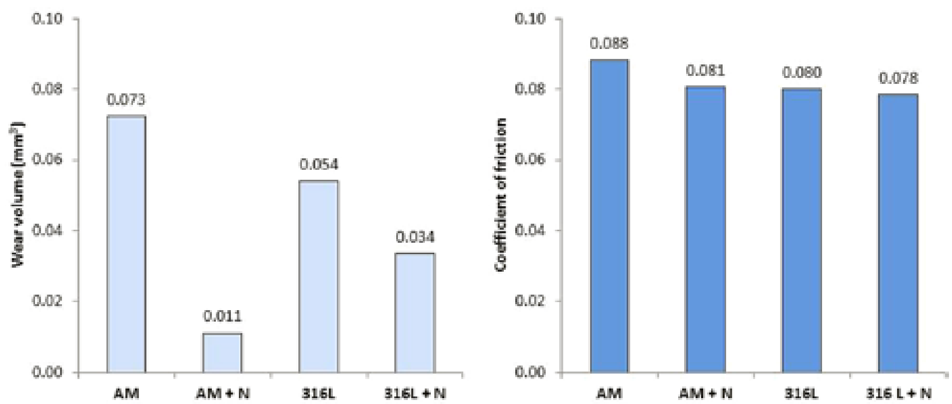


Figure 3: Wear volume (top panel) and coefficient of friction (bottom panel) of the 100Cr6 counter-ball sliding against AM (±N) and 316L (±N) stainless-steel samples [4].

Sample	Average corrosion rate (μm/year)
AM	7.0
AM + N	7.7
316L	10.5
316L + N	3.5

Table 1: Electrochemical parameters determined by potentiodynamic measurements for AM (±N) and 316L (±N) stainless steel samples.

One of the key challenges to the AM technique is that it leads to residual stresses that decrease the mechanical properties of the stainless steel.

Corrosion-testing results

Corrosion testing was calculated using potentiodynamic measurements. Comparison of the materials showed that the corrosion rate was lower for AM 316L than AISI 316L (Table 1) and that after nitriding there was a slight increase in rate for AM 316L and a marked reduction in AISI 316L, which the authors explain is due to the improved barrier properties afforded by the nitriding process.

RELEVANCE TO HTF SECTOR

The main finding of relevance to the heat-transfer sector relates to the hardness, wear, and corrosion of the AM (+N) material vs. the commercially available AISI 316L materials. The AM (±N) material had better hardness than AISI 316L; it had similar frictional wear properties and slightly (in the case of AM + N) worse wear volume performance; and, better corrosion resistance (i.e. AM ± N) than its commercial counterpart. These findings are particularly relevant to the HTF sector from a compatibility perspective and also in terms of offering equivalent material performance. Such findings are important as one of the main factors driving HTF system fatigue and aging is the degradation of the HTF. Indeed, use at high temperature leads to the natural thermal degradation of the fluid, and this can be detected by the formation of short- and long-chain hydrocarbons. In some systems, exposure to air may also accelerate the aging of the HTF, and this is detected as an increase in the acidity of the fluid and corrosion of the system. A further factor that can have an influence is the formation of wear particles that can accumulate in the HTF and lead to internal wear of the pipework and heat in the HTF system. Hence, based on AM 316L, providing equivalent performance to AISI 316L is an important consideration for future research in the HTF area and for potential commercial usage.

BIBLIOGRAPHY

[1] Anon. The Relative Merits and Limitations of Thermal Fluid, Electric and Steam Heat Tracing Systems. Available at: www.sterlco.com [Accessed August 6, 2020].

[2] Anon. The Role of Stainless Steel in Industrial Heat Exchangers.

[3] Zadi-Maad A, Rohib R, Irawan A. Additive manufacturing for steels: a review. IOP Conf. Ser. Mater. Sci. Eng. 2018; 285: 1–8.

[4] Godec M, Donik, Kocijan A, Podgornik B, Skobir Balantič DA. Effect of post-treated low-temperature plasma nitriding on the wear and corrosion resistance of 316L stainless steel manufactured by laser powder-bed fusion. Addit. Manuf. 2020; 32: 101000.

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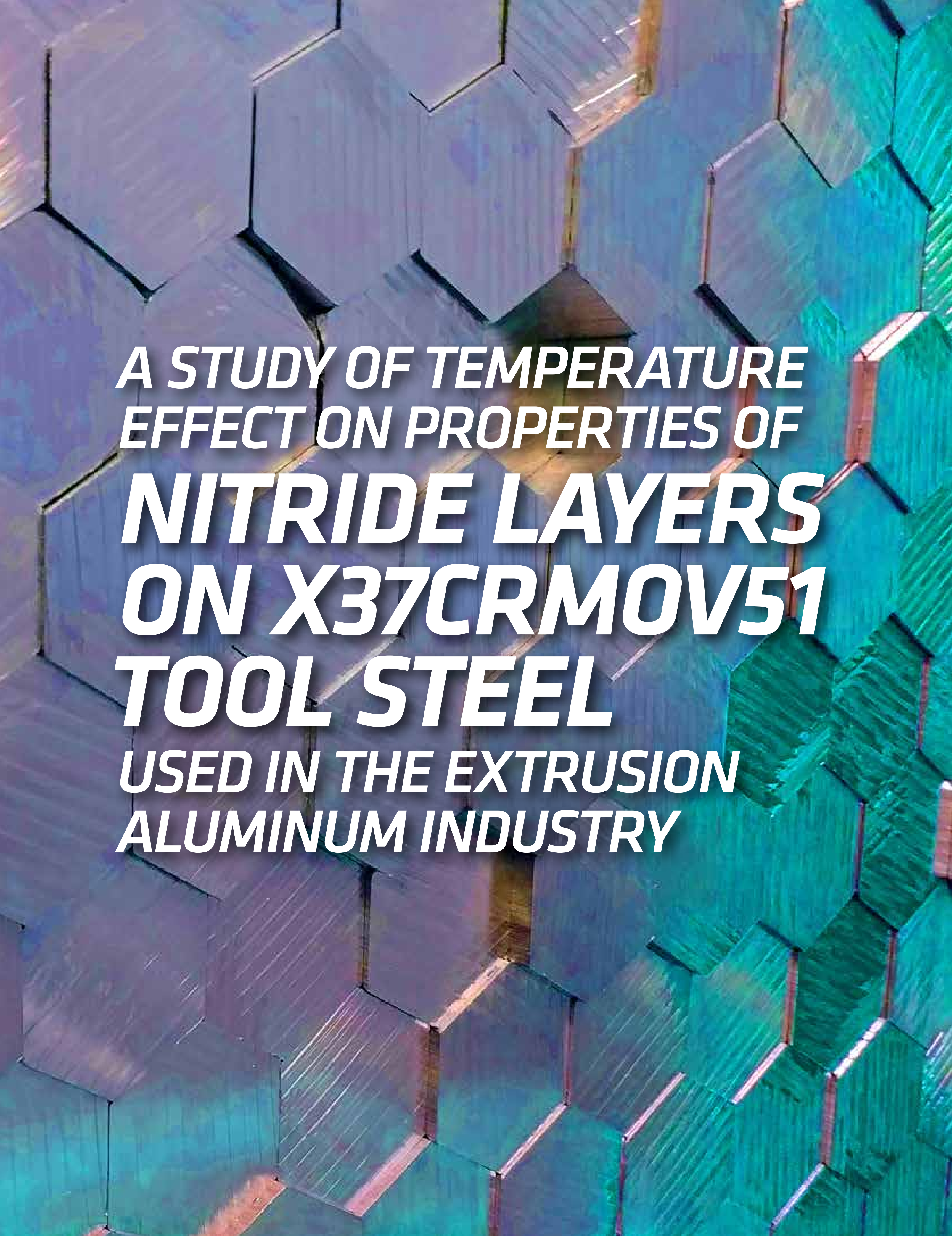

A STUDY OF TEMPERATURE EFFECT ON PROPERTIES OF NITRIDE LAYERS ON X37CRMOV51 TOOL STEEL USED IN THE EXTRUSION ALUMINUM INDUSTRY

After testing samples for structure, hardness, and abrasion immediately after nitriding and again after annealing, it was found that annealing the nitrided samples leads to degradation of the nitride layer, accounting for a decrease of hardness.

By RAFAŁ HUBICKI, MARIA RICHERT, and MARCEL WIEWIÓRA

The paper concerns the effect of annealing time and temperature on the properties of the nitride layer on X37CrMoV51 tool steel used in the extrusion aluminum industry. Samples made from X37CrMoV51 steel were hardened and tempered, and then nitrided at 530°C. After nitriding, the samples were annealed in a furnace at 470°C for 8 hours, 12 hours, 24 hours, 30 hours, and 60 hours, and additionally for 20 hours at 270°C. The samples were tested for structure, hardness, and abrasion immediately after nitriding and again after annealing. It was found that annealing the nitrided samples leads to degradation of the nitride layer, accounting for the decrease of hardness. The annealing of the samples at 470°C for more than 12 hours causes a decrease in mean hardness value from 1,176 HV to 1,103 HV, and annealing the samples more than 30 hours at this temperature leads to a decrease in hardness to 964 HV. The changes in nitrogen content in the white (compound) and diffusion layers and the resulting consequences of changes in phase composition and properties were evaluated. Annealing more than 30 hours at 470°C caused the white layer to disappear and the average nitrogen content in the diffusion layer to decrease to the level of about 5–6 at%.

1 INTRODUCTION

Nitriding of tool surfaces is one of the most commonly used types of heat treatment of tool steels. The nitriding process increases the hardness of the surface layers as well as resistance to abrasion and corrosion [1–4].

The properties achieved by nitriding may change due to the use of the dies and their annealing. During the extrusion process, the die is exposed to high temperatures that affect the surface condition. Before the dies are placed in the press, they are heated, which also affects the condition of the nitride layer.

Dies for extrusion of aluminum alloys are subjected to repeated regeneration by secondary nitriding, which results in multiple high-temperature treatments. The need for regeneration results from the abrasion of the nitrided layer from the surface of the calibrating bearing of the dies during their exploitation.

Nitriding consists in diffusing nitrogen into the surface layer of steel. It is carried out in the temperature range 500–650°C in an ammonia atmosphere. Above 400°C, the ammonia decomposes according to the $NH_3 \rightarrow 3H + N$ reaction. Atomic nitrogen diffuses into the steel and forms nitride phases. At the temperature of 591°C, the nitride layer consists of three phases: ε-Fe_2N nitride, γ′-Fe_4N nitride, and nitrogen ferrite, which contains 0.01% nitrogen at room temperature. At the temperature of 600–650°C, the γ phase is formed, which, when slowly cooled down to the temperature of 591°C, transforms into eutectoid ε + γ′ [5–9].

The hardness of the nitride layer reaches the level of 1,100–1,200 HV and should maintain this level when reheated to working temperatures of 500–600°C. The nitride layer of tempered steel is wear-resistant.

The nitriding process, which lasts from about 20 to 50 hours, produces a layer with a thickness of 0.2–0.4 mm. Increasing the nitriding temperature causes an increase in the thickness of the nitride layer; however, it reduces its hardness, which adversely affects the resistance to abrasion. Literature data indicate that lower nitriding temperature favors high hardness of the nitride layer and good resistance against erosion and corrosion resistance [1–3].

The effect of nitrogen presence in the atomic structure of steel is the formation of nitrides and the interstitial location of nitrogen in the crystal lattice. Depending on the concentration of nitrogen, different stoichiometric nitride compositions can be found. Nitrides as compounds, such as titanium nitride [10] or boron nitride [11], are characterized by high hardness and refractory properties and are used in the production of cutting tool blades, refractory laboratory vessels, and protective coatings. Gallium nitride was used in the production of blue laser [12]. Like some oxides, nitrides can absorb hydrogen and are considered for hydrogen storage, e.g., lithium nitride [13].

Depending on the concentration of nitrogen, there are different stoichiometric nitride compositions in steels. Apart from nitrides formed as a result of the connection of nitrogen and iron, such as Fe_2N, and Fe_4N, CrN nitrides are also formed in steels containing chromium [14–19]. The formation of a CrN phase results in the reduction in the corrosion resistance of the nitride layer in chromium-containing steels. The CrN phase is formed during nitriding above 500°C and occurs frequently when using traditional methods of nitriding [1,2]. CrN precipitations, dissolved in ferrite, are very hard. The temperature increase causes them to undergo coalescence, which leads to the loss of coherence with the lattice and the decrease in hardness, as well as initiate changes in the profile of long-range internal stresses. These changes already take place during nitriding.

Depending on the nitrogen content, iron nitride phases with different structure and properties can be formed. Iron has five nitrides observed at ambient conditions: Fe_2N, Fe_3N_4, Fe_4N, Fe_7N_3, and $Fe_{16}N_2$ [15,19,20]. They are crystalline, metallic solids. Lately, it was put forward that the phase diagram of iron nitrides can be extended further to even more N-rich compounds, such as the γ″-FeN and the γ‴-FeN phases [21].

All iron nitrides are metallic conductors, and they are metastable with respect to decomposition into Fe and N_2. The decomposition is limited by kinetic barriers. Atomic nitrogen can be dissolved in the body-centered cubic (bcc) lattice of α-Fe to a concentration of about 0.4 at% N without much distortion of the lattice. When more than 2.4 at% N is dissolved in pure Fe, the bcc lattice undergoes a tetragonal deformation. In the composition range up to about 11 at% N, the iron nitride compound is called nitrogen martensite α′. This phase has a body-centered tetragonal (bct) structure with lattice parameters depending on the nitrogen content. The N atoms occupy randomly octahedral hollow sites in the Fe sublattice. At saturation, nitrogen martensite has the Fe_8N composition. The α′-Fe_8N can transform into the α″-$Fe_{16}N_2$ phase. In this phase, the N atoms are ordered. It can be formed under special conditions from Fe, however, not in its pure form. The α″-$Fe_{16}N_2$ phase attracted considerable attention because of a possible very high saturation magnetization, reported to vary between 2.4 T and 3.2 T [16]. The next phase of the nitrogen content is the γ′-Fe_4N phase (roaldite), which is cubic, with the Fe sublattice arranged in a face-centered cubic (fcc) structure and nitrogen atoms occupying the body-centered position 1/4. As indicated in the phase diagram, this phase has a narrow composition range around 20 at% N. The lattice parameter is 3.795 Å, and the saturation magnetization was reported to be between 1.8 T and 1.9 T [17]. A saturation magnetization value in this range is slightly lower than the one of pure iron (2.21 T), making this phase somewhat less attractive in comparison with Fe.

The authors of the paper [21] point to the important role of carbon in the process of phase changes in the nitride layer and its influence on the internal stress in this zone. Carbon diffusion implies a complex precipitation sequence and a thermodynamic evolution that modify the volume change during nitriding. The transformation of initial carbides into nitrides decreases the kinetics of nitriding and is counteracted by the precipitation of cementite. Surface decarburization involves a decrease in the volume fraction of cementite during nitriding, leading to an unloading of the surface and thus reducing residual stresses. During nitriding, a surface was subject to mechanical loading-unloading through volume changes. The distribution of residual stresses is mainly governed by the thermochemical modifications due to nitrogen and carbon diffusion.

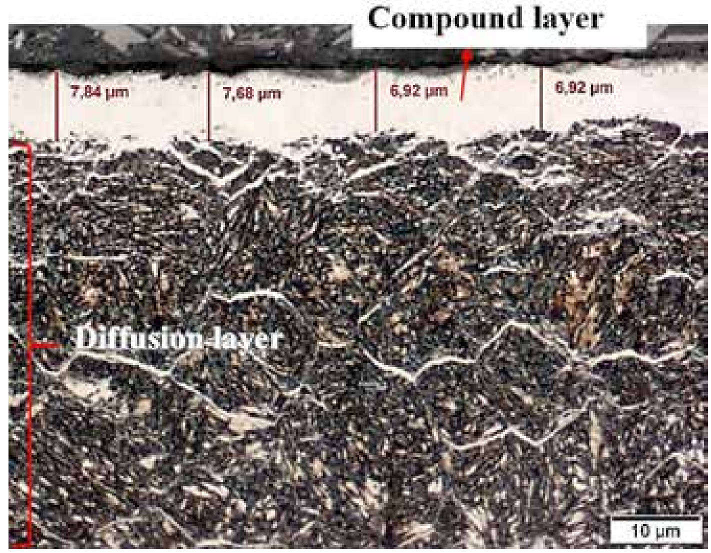

Figure 1: White layer in nitrided Nitromax furnace samples; microstructure of 1.2344 tool steel after gas nitriding shown though an optical microscope; white layer thickness ~7 µm, diffusion layer ~70 µm.

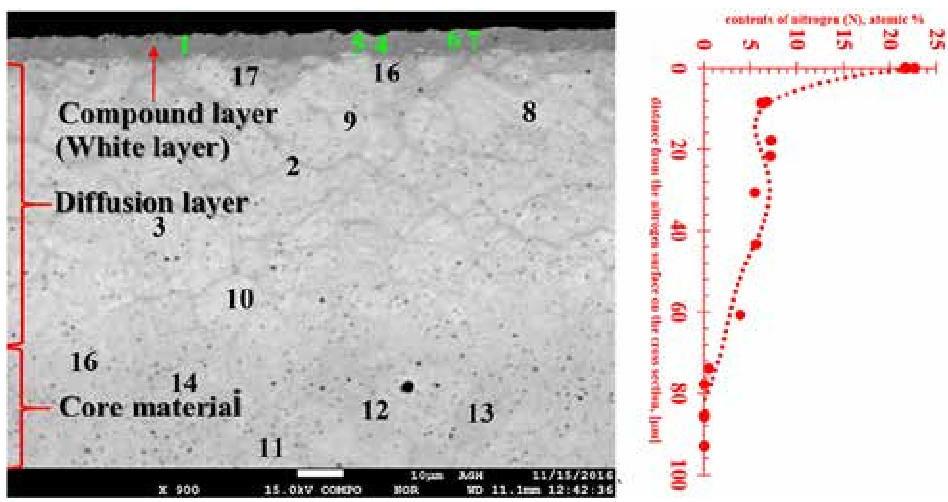

Figure 2: Point analysis of the chemical composition of: the white layer – points 1, 4-7; the diffusion layer – points: 2, 3, 8, 9, 10, 16, and 17; and the steel matrix – points 11-14 in 1.2344 steel after gas nitriding.

Studies show the abrasion resistance of the nitride layer depends on the type of nitriding method [22]. Studies by G. Kugler et al. [23] have shown the presence of a compound (white) layer protects the surface of dies against chemical reaction with hot aluminum [24]. It was found that annealing of the ε-Fe_3N phase leads to the precipitation of the γ′-Fe_4N phase. In this paper, it was also found that long annealing of ε phase causes its homogenization.

In general, it should be emphasized that any time a surface-nitrided tool is exposed to high temperatures, it leads to changes in the nitride layer. In combination with the changes that occur in the substrate, consisting in lowering the density of defects (recovery, polygonization) and the precipitation or decomposition of carbides, as well as their coagulation, this affects the properties of the nitride layer. In particular, the hardness and abrasion resistance of the nitrided surface change. Reducing these properties reduces the life of the dies and increases production costs.

The scope and scale of changes affecting the durability of the dies is of crucial importance due to the practice of using the dies in industry. From this point of view, the more stable the hardness of the nitrided layer is, the better the prognosis of the durability and utility of the die.

Continuous development of the aluminum market causes the demand for dies to increase. According to the prediction of the International Energy Agency, between 2023 and 2030, the demand for aluminum will increase by more than 50 percent, due to, among other things, the rapid development of LED lighting and the development of the automotive industry [25]. The largest aluminum products' production plant in Poland is Grupa Kęty S.A. S.A., which is a company with a long tradition [11]. Grupa Kęty S.A. assumes that, by 2019, it will become the leader in the production of aluminum profiles in Poland with sales of 1,364 million PLN in the Polish aluminum market [26].

The development of the aluminum industry generates the development of production and heat treatment of dies necessary for the production of aluminum profiles. Due to the importance of the die durability issue, the nitriding process is constantly being improved by companies producing nitriding furnaces. Therefore, all research on this subject contributes to the broadening of the knowledge on this subject and to the improvement of the nitriding technology.

In this paper, the influence of temperature on the properties of the nitride layer of tool steel X37CrMoV51 (1.2344 tool steel) was analyzed. Annealing was carried out for different time periods (8-60 hours), and the influence of the given heat-treatment conditions on the structural effects and properties of the nitride layer was evaluated.

2 MATERIALS AND METHODS

The tested samples were nitrided in a Nitromax furnace under indus-

	N	Mo	Fe	V	Cr	Kind of Nitride Layer
			Atomic %			
2	5.442	0.697	84.946	0.961	5.237	Diffusion layer
3	5.532	0.703	85.036	0.980	5.432	
4	21.702	0.499	70.824	0.582	4.606	Compound layer (white layer)
5	21.563	0.557	70.355	1.220	4.572	
6	22.615	0.488	69.383	0.627	5.062	
7	21.513	0.514	71.019	0.577	4.587	
8	7.201	0.601	83.927	0.727	5.295	Diffusion layer
9	7.117	0.597	84.045	0.698	5.256	
10	3.823	0.693	86.829	0.780	5.528	
11	0.000	0.695	90.185	0.887	5.829	Core material
12	0.000	0.710	90.165	0.961	5.750	
13	0.000	0.721	90.287	0.901	5.635	
14	0.000	0.717	90.171	0.906	5.797	
15	0.452	0.737	89.747	1.009	5.709	Boundary between diffusion layer and core material
16	6.698	0.583	84.632	0.761	5.264	Diffusion layer
17	6.117	0.635	84.690	0.715	5.684	

Table 1: Results of chemical composition analysis in the points marked in Figure 2.

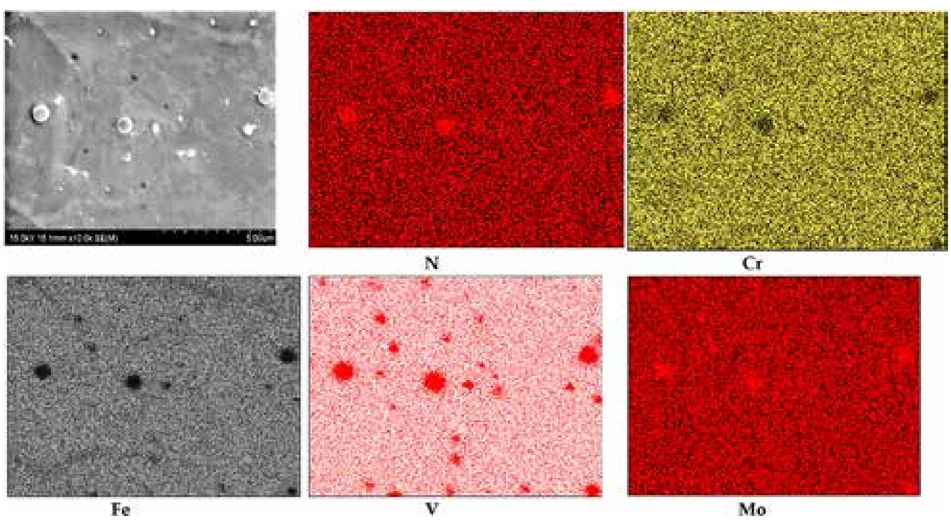

Figure 3: Map of elemental distribution in the white layer of the nitrided sample.

trial conditions.

Samples made from X37CrMoV51 steel were hardened and tempered and then nitrided at 530°C, according to Grupa Kęty S.A.'s (Kęty, Poland) proprietary technology based on the NITREG technology, under conditions in which industrial dies in Grupa Kęty S.A. are nitrided. During primary nitriding, a 120 to 140 μm thick diffusion layer should be formed on the dies. The thickness of the white layer should be between 4 and 6 μm, and the hardness should be higher than 1,000 units.

After nitriding, the samples were annealed in a furnace at 470°C for 8 hours, 12 hours, 24 hours, 30 hours, and 60 hours, and additionally for 20 hours at 270°C. The samples were tested according to the following procedures for structure, hardness, and abrasion resistance immediately after nitriding and again after annealing.

The research was carried out on cross sections. After cutting out the sample, it was sanded with grade #300 and #1200 abrasive papers and polished with diamond paste with grain sizes of 9 μm, 3 μm, and 1 μm. The final polishing was carried out using the silica suspension OP-S according to Struers company procedures. In the next step, the samples were etched in Nital reagent with the following composition: 5 ml HNO_3 + 100 ml C_2H_5OH.

The microstructure of the samples was examined using the Olympus GX-51 optical microscope (Cracow, Poland) and the Hitachi SU-70 scanning electron microscope (Cracow, Poland) equipped with Energy Dispersive X-Ray Analysis (EDX).

The microhardness of the nitride layer was examined using the Shimadz HMV-G apparatus (Cracow, Poland) by means of Vickers' method with the load of 0.9807 N.

Chemical analyses in the microarea of nitrided steel and iron oxides formed as a result of gas nitriding were carried out using an electron probe microanalyzer Jeol SuperProbe JXA-8230 (Cracow, Poland) equipped with Wavelength Dispersive X-ray analysis (WDS). The tests were performed in the Critical Elements Laboratory of AGH-KGHM at the Faculty of Geology, Geophysics and Environmental Protection of the AGH University of Science and Technology in Krakow. Investigations of nitrided steel were carried out with the use of an electron probe microanalyzer with the acceleration voltage of 15 kV and the amperage of 50 nA, whereas, during the measurements of iron oxides, the amperage was 40 nA. The time of analysis of each element lasted 20 seconds in peak maximum position and 10 seconds in background position before and after the peak. The beam size was <1 μm. The following lines and standards were used for steel analysis: BN (NKα), Fe (FeKα), Mo (MoLα), V (VKα), Cr (CrKα). The following lines and standards were used for the analysis of iron oxides: BN (NKα), fayalite (FeKα), Mo (MoLα), V (VKα), Cr_2O_3 (CrKα).

3 RESULTS

Studies on the structure of samples directly after nitriding showed that a white (compound) layer was formed on their surface (Figure 1). The thickness of this layer was estimated at about 7-8 μm, while the depth of the diffusion layer was about 70 μm (Figure 1).

To estimate the nitrogen content in the studied layers, the EDX method of chemical composition analysis with a scanning microscope was applied. The locations where the chemical composition was determined are shown in Figure 2, and quantitative results of chemical composition tests are shown in Table 1. The high nitrogen level and structural phase contrast identified a white (compound) layer.

The white layer contained more than 21 at%. of nitrogen, which means the range of occurrence of $\gamma'+\varepsilon$, or ε-Fe_2N nitride, γ'-Fe_4N nitride and nitrogen ferrite, which contains 0.01% nitrogen at room temperature (Figure 3). Table 1 also shows results indicating the presence of a diffusion layer with nitrogen in the range 3.9-7.2 at%. These values indicate the extent of the presence of eutectoid mixture $\alpha+\gamma'$, consisting of phases: γ'-Fe_4N nitride and α-nitride ferrite.

The nitrogen profile attached to Figure 2 clearly shows the very high nitrogen content in the near-surface layer decreases rapidly and already at a distance of about 10 μm from the sample surface, then at a distance of about 80 μm, it reaches the zero level. This is the indicator of the boundary of the diffusion layer. Therefore, the thickness of the hard, nitride layer is relatively small, and the friction forces cause its rapid wear, which makes it necessary to regenerate the layer after a specified period of using the tool.

The results of WDS analysis of the chemical composition of the white layer (compound layer) in the form of elemental distribution maps are presented in Figure 3. In the maps, the position of nitrogen concentration appeared at the same place as the position of Fe, Cr, V, and Mo. The average nitrogen content in the white layer was about 21.84 at% and in the diffusion layer it was about 5.82 at%. The average in both layers' content of nitrogen was found to be 13.82 at%. The Cr content was estimated in white layer at about 4.71 at%, in the diffusion layer at about 5.35 at%, and in the core material at about 5.75 at% — for an average value of about 5.27 at%. The content of Mo in the white layer was about 0.51 at%, in the diffusion layer about 0.66 at%, and in the core material 0.71 at%. Generally, the content of Mo was 0.63 at%. The V content in the white layer was about 0.75 at% in the diffusion layer 2.03 at% and in the core material about 1.14 at%. The average V content was about 1.31 at%.

The existence of Cr, V, and Mo in the same positions on the chemical composition maps from WDX measurement (Figure 3) suggests the probability of complex nitride precipitation. In such a case, chromium surely is dissolved in iron nitrides. It was shown that in ternary alloy systems where the crystal structures of the binary boundary nitrides are similar and the interaction parameter difference of the nitride forming elements is moderate, mixed ternary nitrides can develop [27]. Increasing numbers of ternary nitrides, $A_xM_yN_z$, have been described in recent years, and these exhibit a great richness of structure and physical property [28,29].

After nitriding, the samples were annealed at 470°C for 3 hours (Figure 4a,b), 8 hours (Figure 5a,b), 30 hours (Figure 6a,b), and 60 hours (Figure 7a,b). As a result of annealing, the white layer was degraded. Microstructure observations show the thickness of the white layer decreased as the annealing time increased, and for the annealing time of 30 hours and 60 hours, it disappeared altogether.

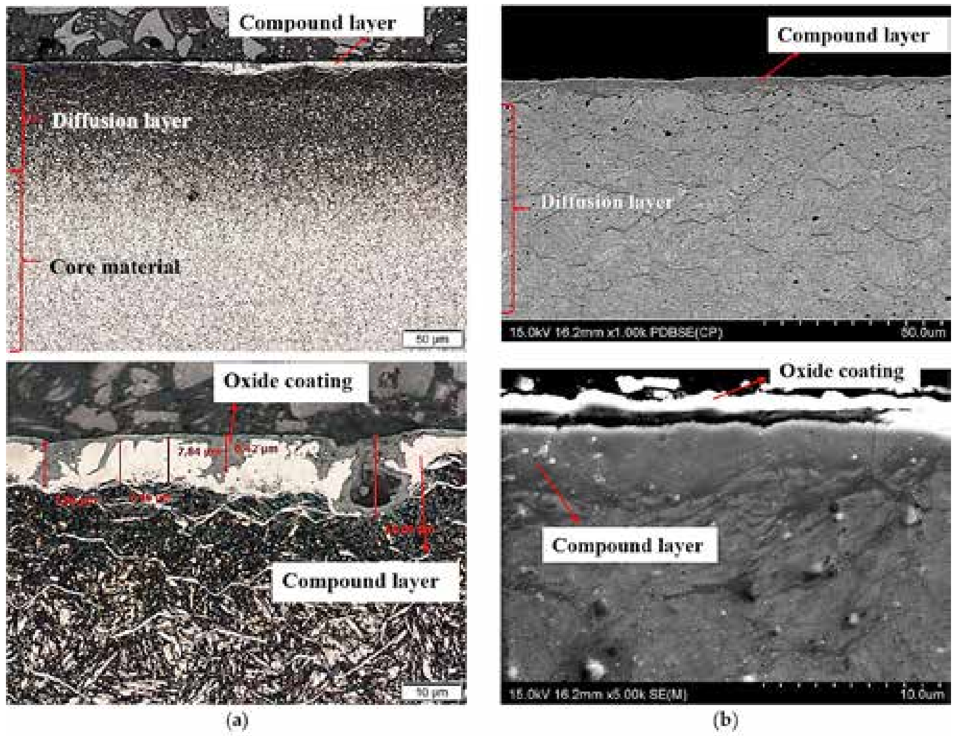

Figure 4: (a) Microstructure of WCLV steel after gas nitriding at Grupa Kęty S.A. and annealing for 3 hours at 470°C, show through an optical microscope (OM). Thickness of white layer ~7 μm and diffusion layer ~70 μm. Visible on the surface is the corrosive layer formed during annealing, which results in degradation of the white layer (b) Microstructure of WCLV steel after gas nitriding in Grupa Kęty S.A. and annealing for 3 hours at 470°C, shown though a scanning microscope (SEM). Thickness of white layer ~7μm, diffusion layer ~70 μm, and corrosion ~2 μm.

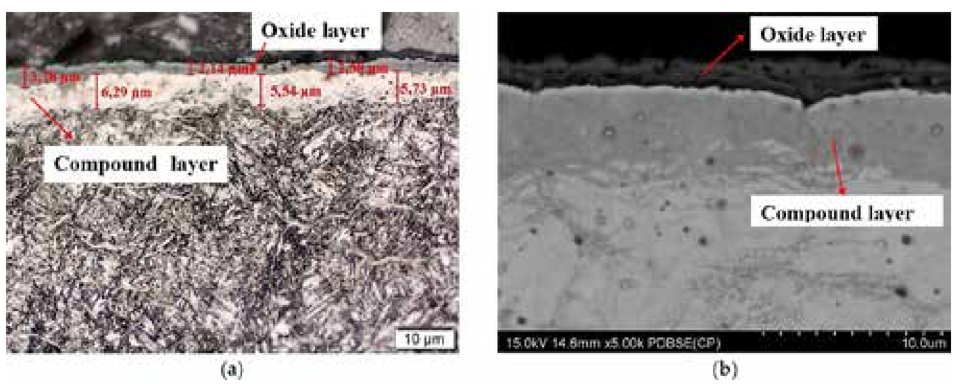

Figure 5: (a) Microstructure of WCLV steel after gas nitriding in Grupa Kęty S.A. and annealing for 8 hours at 470°C, shown with an optical microscope. Thickness of the white layer ~6 μm, diffusion layer ~70 μm and corrosion layer ~2 μm. The corrosion layer visible on the surface was formed during annealing, and it causes degradation of the white layer. (b) Microstructure of WCLV steel after gas nitriding in Grupa Kęty S.A and annealing for 8 hours at 470°C, shown with a scanning microscope. Thickness of white layer ~6 μm, diffusion layer ~70 μm, and corrosion layer ~2 μm.

The width of the diffusion layer was observed to grow and equaled about 70 μm for 3 hours and 8 hours of annealing, about 80 μm for 30 hours, and about 100 μm for 60 hours.

The oxidation of nitride samples appeared locally after annealing for 3 hours at 470°C (Figure 4a) and increased with annealing time prolongation. The oxide growth at temperatures between 423 K and 623 K could be described consistently with the oxidation model of Fromhold and Cook (FC) [30]. It describes the initial oxidation of metals (0-20 nm). In the FC theory, the reaction between metal and oxygen takes place at the growing oxide/oxygen interface, requiring both metal ions and electrons to move through the oxide layer to the surface. The transport of electrons can proceed by two mechanisms: tunneling and thermionic emission. For temperatures below 420 K, there is virtually no thermionic emission at the metal-oxide interface, and electron tunneling is the dominant process. According to the FC formalism, at T ≤ 420 K, electron transport proceeds by tunneling through the oxide layer and therefore the limiting film thickness should be nearly independent of the oxidation temperature. However, the measurements show the saturation thickness does depend on the temperature and varies between 8.5×10^{15} O atoms/cm^2 at room temperature (RT) and 15×10^{15} O atoms/cm^2 at 395 K [31,32]. A two-layer system is formed, with a first layer

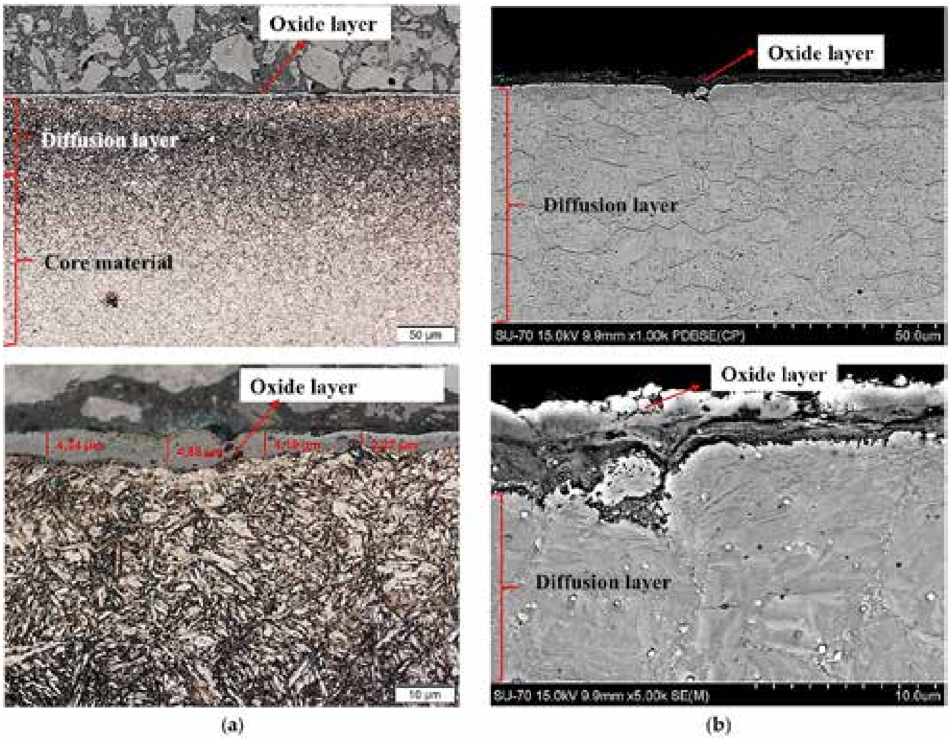

Figure 6: (a) Microstructure of WCLV steel after gas nitriding in Grupa Kęty S.A. and annealing for 30 hours at 470°C, shown with an optical microscope. No visible white layer. Layer thickness of diffusion layer ~80 µm and corrosion layer ~4 µm. (b) Microstructure of WCLV steel after gas nitriding in Grupa Kęty S.A and annealing for 30 hours at 470°C, shown with a scanning microscope. No white layer. Layer thickness of diffusion layer ~80 µm and corrosion layer ~4 µm.

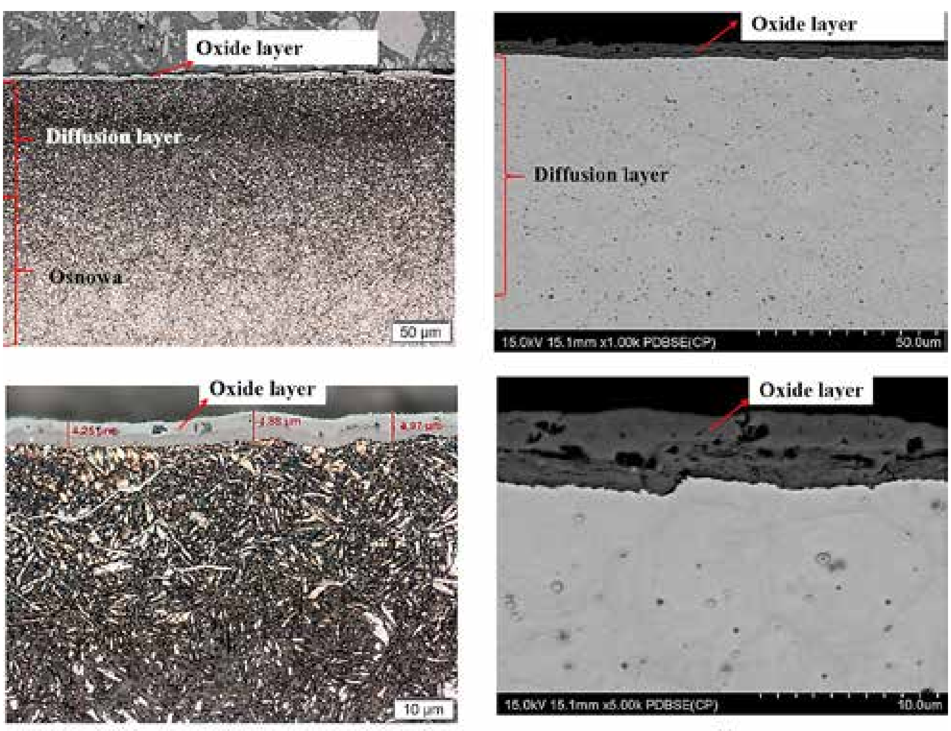

Figure 7: (a) Microstructure of WCLV steel after gas nitriding in Grupa Kęty S.A. and annealing for 60 hours at 470°C, shown with an optical microscope. No white layer. Layer thickness of diffusion layer ~100 µm and corrosion layer ~4.5 µm. (b) Microstructure of WCLV steel after gas nitriding in Grupa Kęty S.A. and annealing for 60 hours at 470°C, shown with a scanning microscope. No white layer. Layer thickness of diffusion layer ~100 µm and corrosion layer ~4.5 µm.

containing Fe^{2+} only, and a top layer containing both Fe^{3+} and Fe^{2+}. The growth of the second layer starts at an oxygen coverage of 4.0×10^{15} O atoms/cm^2 and consists of $Fe_{0.77}O$ (which is probably a mixture of Fe^O and γ-Fe_2O_3). At higher oxidation temperatures, the relative fraction of Fe^{3+} in the formed oxide decreases. The oxide layer formed in O_2 at 473 K consists of Fe^{2+} only. The decrease of the oxidation rate coincides with the formation of an oxide layer containing Fe^{3+}. Upon annealing, Fe^{3+} is reduced to Fe^{2+}, while the displaced Fe^0 is oxidized to Fe^{2+}. For larger oxide thicknesses (L > 3 nm) and higher temperatures (T > 420 K), the dominant electron transport processes thermionic emission. For higher temperatures and larger oxide thicknesses, the thermionic emission of electrons is rate-limiting. For lower temperatures and smaller oxide thicknesses, the presence of Fe^{3+} drastically decreases the oxidation rate. The reduction rate of Fe^{3+} to Fe^{2+} increases with increasing temperature. An important feature of the FC theory is the concept of coupled currents: The net electrical current across the oxide layer is zero. At sufficiently high-oxygen pressures, transport of either electrons or metal ions is rate-limiting.

The oxidation of nitride steel was investigated by Yang Li and all [33]. The iron oxide phases of hematite (Fe_2O_3) and magnetite (Fe_3O_4) through the post-oxidizing treatment at 400°C and 450°C was found. The hematite has been also identified in work [34] after the post-oxidation of plasma nitriding AISI 4140 steel. In contrast, in [35], after oxidation of nitride layer at 480°C to 500°C, Fe_3O_4 (magnetite) was reported. It was also described that the precipitation of CrN or Cr in complex nitride precipitations at 500°C removed Cr from the solid solution and adversely affected the oxidation performance at this temperature [35]. Formation of CrN and γ'-Fe_4N causes the corrosion resistance of the nitrided layer to decrease [36]. The nitrogen atoms occupy similar types of surface sites as the oxygen atoms [37] Displacement of N atoms from the surface into the bulk by interaction with gaseous O_2 will be energetically rather favorable. The bulk diffusion coefficient of N in pure Fe has, at 900 K, a value of about 10^{-7} cm^2/s and an activation energy of 18.9 kcal/mole. Extrapolation to room temperature yields a mean displacement by diffusion of about 5 A within 30 minutes. This process will, however, certainly be strongly accelerated by the rearrangement of the Fe atoms in the course of oxide formation (oxygen chemisorption on Fe(100)), which was found to cause an expansion of the topmost layers, as well as by the energy release associated with the oxygen attack, so that displacement of the N atoms, even at room temperature, becomes feasible. On the other hand, the further growth of the oxide will certainly be retarded by previous formation of a nitride layer in the surface region — this is the well-known anticorrosive effect.

The research showed that, as a result of long annealing times, the surface hardness of the samples decreased by about 200-250 units (Figure 8) in relation to the hardness of the original nitrided sample. The hardness results shown in Figure 8 can be divided into three groups, as presented at Figure 9. The highest hardness (average 1,176 HV) is found in samples annealed for 3, 8, and 12 hours at the temperature of 470°C. The group of samples annealed for 20 hours at 270°C have the average hardness 1,103 HV. The lowest hardness was found in samples annealed for 30 and 60 hours at 470°C with the average hardness 964 HV. The difference between the highest and lowest hardness is 212 HV.

Abrasion tests revealed a correlation between the hardness level and weight loss in the abrasion test. It was found that the lower the hardness, the more abrasive the surface of the samples was (Figure 10).

The analysis of nitrogen content in the white and diffusion layers was based on the results of EDX and WDS chemical composition tests. Figure 11 summarizes the data on nitride content in white and diffusion layers. The white layer contained on average about 19.4% atomic of nitrogen, and this level of nitrogen is stable in samples annealed in the range of 3 to about 12 hours at 470°C. Above this time of annealing, the white layer disappeared. For the annealing times of 30 hours and above, no white layer was found. The nitrogen content in the white layer suggests the occurrence of $\gamma' + \varepsilon$ phases. When the content of nitrogen decreases, the aforementioned phases do not exist. It should be assumed the disappearance of the white layer occurred as a result of the decrease in nitrogen content, which diffused deep into the substrate, as evidenced by the increase in the thickness of the diffusion layer.

The diffusion layer contained about 8.1% atomic of nitrogen in samples annealed for 8–12 hours (Figure 11). Samples annealed for more than 12 hours showed an average nitrogen content reduced to about 5.6% atomic. Reduced nitrogen content in the diffusion layer predicted the presence of phases $\alpha + \gamma'$.

4 DISCUSSION

Coatings and layers produced by various surface engineering methods reveal a variety of structures and thicknesses. This is due to the mechanisms of forming coatings and layers. Nitriding is a specific surface treatment in which the top layer of a tempered tool is saturated with nitrogen at high temperatures. The effect of nitrogen in the atomic structure of steel is the formation of nitrides and the interstitial location of nitrogen in the crystal lattice. Depending on the concentration of nitrogen, different stoichiometric nitride compositions can be found. Apart from nitrides formed as a result of the compound of nitrogen and iron, i.e., nitrides such as Fe_2N and Fe_4N, moderate mixed ternary nitrides can also develop. In the conducted studies, the searching of nitride particles were performed by EDX and WDS measurement of chemical composition in points and chemical composition maps. We found Cr, Mo, Fe, V, and N concentration in the same places, which suggests formation in or quaternary phase [38,39]. The investigation in work shows that at lower Cr/Mo ratio, hexagonal $CrMoN_2$ precipitation occurred.

The presence in the nitride test layer of a hard nitrogen phases occur near the surface of the samples is significant for die resistance to abrasion. Nitrogen phases especially increase the hardness, which translates into higher abrasion resistance [40]. Reducing the surface nitrogen content in the white layer leads to phase changes and loss of high hardness [41,42]. As a result of experimental annealing, the initial hardness of the nitride layer, amounting to approximately 1,190 HV, was reduced by approximately 210 units (Figure 8). From a practical point of view, reducing the hardness

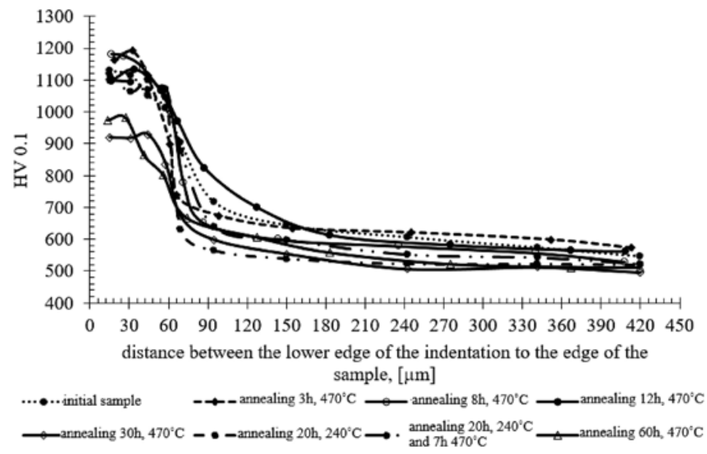

Figure 8: Hardness change profiles as a function of annealing time at 470°C.

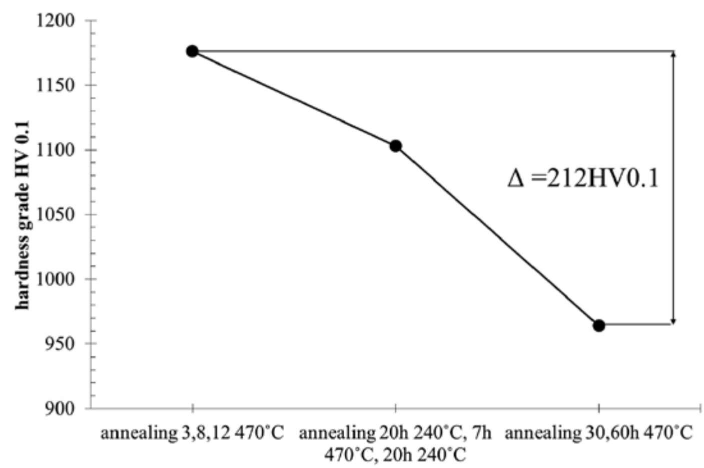

Figure 9: Mean hardness graph of three groups of annealed nitrided WCLV steel samples, measured at 15 µm from the sample surface. HV = 1176 — mean hardness of sample group annealed at 3, 8, and 12 hours at 470°C; HV = 1103 — mean hardness of sample group annealed for 20 hours at 240°C, 7 h at 470°C and 20 h at 240°C; and HV = 964 — mean value of hardness for annealing at 30 h and 60 hours at 470°C.

below 1,000 HV disqualifies aluminum extrusion dies for further use. During the annealing at 470 C, the oxidation of the sample surface develops. The thickness of the oxide layer increases with annealing time prolongation. However, above 8 hours of annealing, it becomes almost stable. Experimental investigations show a "parabolic law" of oxide layer growth [43]. Dwivedi D., Lepková K. and Becker T. [44] point out the importance of texture in the corrosion process. Robert E. Melchers [45] presented different models of corrosion loss starting from different assumptions and showed parabolic and linear lows of oxidation. The oxidation zone containing (Mn,Fe)O and $(Mn,Cr,Fe)_3O_4$ oxides in annealed Fe–1.9Mn–1.6Cr steel was investigated by Mao, W., Ma, Y. and Sloof, W.G [46]. It was found the penetration depth of oxides along grain boundaries is much larger (by a factor of two or more) than that of internal oxides formed inside grains. They also found a parabolic rate law of oxidation. In relation to obtained results, it should be assumed the parabolic oxide layer grows and oxidation stabilizes in the range of 30 hours to 60 hours of annealing.

It should be mentioned that the presence of nitride and carbide phases in tools for which no additional heat treatment is applied is beneficial due to the high surface hardness. However, if the surface of the die is designed to be covered with an additional coating, e.g., PVD — Physical Vapor Deposition, the heat treatment should be car-

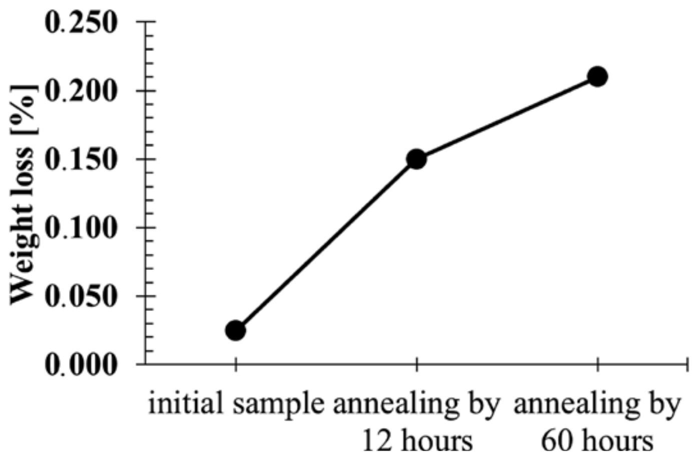

Figure 10: The weight loss of initial sample (0.025), sample annealed for 12 hours in 470°C (0.15) and samples annealed for 60 hours at 470°C (0.21).

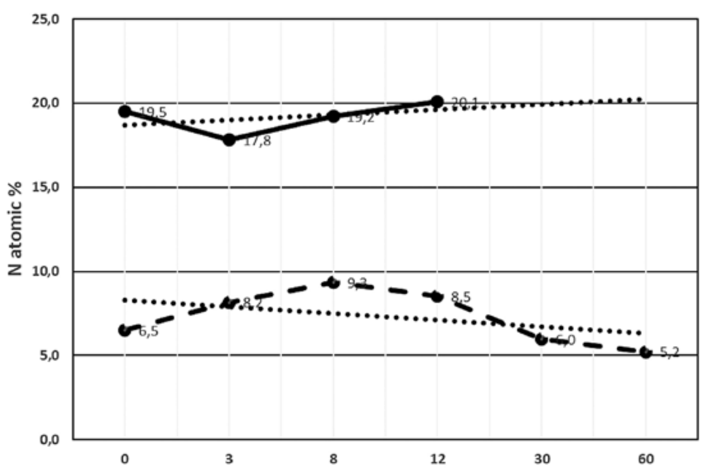

Figure 11: Mean nitrogen content in the white and diffusion layer in the samples after nitriding and annealing for 3 to 60 hours at the temperature of 470°C, measured at the same place from surface. The upper line shows mean value of nitrogen in white layer. The dotted line indicates estimation course in annealing time. The lower line indicates mean value of nitrogen content in diffusion layer and the dotted line indicates the tendency to decreasing nitrogen content with the extension of annealing time.

ried out in such a way that no white layer is formed. There should only be a diffusion zone characterized by maximum effective thicknesses and devoid of carbide precipitations at the grain boundaries of the former austenite [42]. It can therefore be concluded that the design and implementation of the nitriding process and its effects will depend on the purpose for which the tools are used.

The life cycle of the dies includes periods at elevated temperatures (470°C and 520°C) and periods at room temperature. Cyclic changes in the working temperature during die life of the die make it subject to processes of structural and phase changes. This results in changes of properties and, ultimately, after the loss of the required hardness level, the need for regeneration through secondary nitriding.

The substrate is also subject to changes under the influence of temperature. There are recovery processes that reduce dislocation densities and other lattice defects. The processes of precipitation coagulation take place. Precipitations that were coherently bound to the matrix lose their coherence, which results in a decrease of hardness. The phenomena of structure restoration, combined with changes in the morphology of the precipitations, lead to unfavorable changes of properties in terms of die exploitation.

5 CONCLUSIONS

On the basis of the research carried out, it was found that:

› **1.** Annealing of the nitrided samples leads to degradation of the nitride layer and the decrease of hardness.

› **2.** Annealing of the samples at 470°C for more than 12 hours causes a decrease in mean hardness value from 1,176 HV to 1,103 HV, and annealing the samples more than 30 hours at this temperature leads to a decrease in hardness to 964 HV.

› **3.** Tests have shown a decrease in abrasive resistance as the annealing time increases.

› **4.** Annealing more than 30 hours at 470°C caused the white layer to disappear and the average nitrogen content in the diffusion layer to decrease to the level of about 6 at%.

AUTHOR CONTRIBUTIONS

Conceptualization, R.H., M.R. and M.W.; Investigations R.H., M.R. and M.W., Writing-Original Draft: M.R., Preparation, R.H., M.R. and M.W. All authors have read and agreed to the published version of the manuscript.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

REFERENCES

[1] Yang, M. Nitriding–Fundamentals, Modeling and Process Optimization. Ph.D. Thesis, Worcester Polytechnic Institute, Worcester, MA, USA, April 2012.

[2] Conceição Rocha Lima Cesconettoa, M.; Ribeiro Franco, A., Jr.; Aparecido Vieiraa, E. Improving the Abrasive Wear Resistance of a Microalloyed Steel by Plasma Nitriding. Mater. Res. 2015, 18, 334–340. [CrossRef]

[3] Aydin, H.; Bayram, A.; Topcu, S. The effect of duplex surface treatment on erosion performance of QRO 90 Supreme steel. Mater. Sci. 2013, 19, 19–24.

[4] Xu, X.; Wang, L.; Yu, Z.; Qiang, J.; Hei, Z. Study of microstructure of low-temperature plasma nitride AISI 304 stainless steel. Metall. Mater. Trans. A 2000, 21A, 1193–1199. [CrossRef]

[5] Kooi Bart, J.; Somers Marcel, A.J.; Mittemeijer Eric, J. An Evaluation of the Fe-N Phase Diagram Considering Long-Range Order of N Atoms in γ′Fe4N1-x and ε-Fe2N1-z. Metall. Mater. Trans. A 1996, 27A, 1063–1071. [CrossRef]

[6] Eom, J.Y.; Shankar Rao, V.; Kwon, H.S.; Nam, K.S. Experiments and modeling study on growth behavior of Cr-nitrides formed on electroplated hard Cr during ion-nitriding. J. Mater. Res. 2003, 18, 861–867.

[7] Widenmeyer, M.; Hansen, T.C.; Meissner, E.; Niewa, R. Formation and Decomposition of Iron Nitrides Observed by in situ Powder Neutron Diffraction and Thermal Analysis. J. Inorg. Gen. Chem. 2014, 640, 1265–1274. [CrossRef]

[8] Bjørsom, H.B. Investigation of the Compound Layer and Diffusion Zone of Pulsed Plasma Nitrided 51CrV4-Steel. Master's Thesis, Energy and Nanotechnology Department of Physics, University of Oslo, Oslo, Sweden, September 2013. Available online: https://www.duo.uio.no/bitstream/handle/10852/41371/Bjorsom_ Masteroppgave.pdf?sequence=1 (accessed on 30 September 2013).

[9] Díaz-Guillén, J.C.; Vargas-Gutiérrez, G.; Granda-Gutiérrez, E.E.; Zamarripa-Piña, J.S.; Pérez-Aguilar, S.I.; Candelas-Ramírez, J.; Álvarez-Contreras, L. Surface Properties of Fe4N Compounds Layer on AISI 4340 Steel Modified by Pulsed Plasma Nitriding. J. Mater. Sci. Technol. 2013, 29, 287–290. [CrossRef]

[10] Van Hove, R.P.; Sierevelt, I.N.; van Royen, B.J.; Nolte, P.A. Titanium-Nitride Coating of Orthopaedic Implants: A Review of the Literature. J. List Biomed. Res. Int. 2015, 2015, 485975. [CrossRef]

[11] Caldwell, J.D.; Aharonovich, I.; Cassabois, G.; Edgar, J.H.; Gil, B.; Basov, D.N. Photonics with hexagonal boron nitride. Nat. Rev. Mater. 2019, 4, 552–567. [CrossRef]

[12] Oliver, E.A. Critical Assessment 23: Gallium nitride-based visible light-emitting diodes. Mater. Sci. Technol. 2016, 32, 737–745. [CrossRef]

[13] Boukamp, B.A.; Huggins, R.A. Lithium ion conductivity in lithium nitride. Phys. Lett. 1976, 58, 231–233. [CrossRef]

[14] Drewnicka, D. Advanced investigation methods of nitride layers after heat treatment. Inz˙ynieria Powierzchni (Surf. Eng.) 2012, 2, 14–18.

[15] Borsa, D.M. Nitride-based Insulating and Magnetic thin Films and Multilayers. Available online: https://www.rug.nl/research/portal/en/publications/nitridebased-insulating-and-magnetic-thin- films-and-multilayers(a667d5ad-8d0b-4eda-80c7-130ef5315665).html (accessed on 10 March 2004).

[16] Yamashita, S.; Masubuchi, Y.; Nakazawa, Y.; Okayama, T.; Tsuchiya, M.; Kikkawa, S. Crystal structure and magnetic properties of "α"-Fe16N2" containing residual α-Fe prepared by low-temperature ammonia nitridation. J. Solid State Chem. 2012, 194, 76–79. [CrossRef]

[17] Xiong, X.C.; Redjaïmia, A.; Gouné, M. Transmission electron microscopy investigation of acicular ferrite precipitation in γ'-Fe4N nitride. Mater. Charact. 2010, 61, 1245–1251. [CrossRef]

[18] Buschow, K.H.J.; Robert, W.; Cahn, P.V. Encyclopedia of Materials: Science and Technology; Elsevier Ltd.: Amsterdam, The Netherlands, 2001.

[19] Lengauer, W.; Eder, A. Nitrides: Transition Metal Solid-State Chemistry, Encyclopedia of Inorganic Chemistry, 2nd ed.; King, R.B., Ed.; John Wiley & Sons, Ltd.: Chichester, UK, 2005; Volume VI, pp. 3515–3531.

[20] Litasov, K.D.; Shatskiy, A.; Ponomarev, D.S.; Gavryushkin, P.N. Equations of state of iron nitrides ε-Fe3Nx and γ-Fe4Ny to 30 GPa and 1200 K and implication for nitrogen in the Earth's core. J. Geophys. Res. Solid Earth 2017, 122, 3574–3584. [CrossRef]

[21] Jegoua, S.; Barrallier, L.; Kubler, R. Phase transformations and induced volume changes in a nitrided ternary Fe–3%Cr–0.345%C alloy. Acta Mater. 2010, 58, 2666–2676. [CrossRef]

[22] Runge, J.M.; Pomis, A.J. Presented at the XII Ebrats Brasilian Surface Treatment Meeting and II Latin–American Interfinish, Sao Paulo, Brazil, 10 May 2006.

[23] Kugler, G.; Vecko–Pirtovsek, T.; Tercelj, M. Wear behavior of nitrided microstructures of aisi h13 dies for hot extrusion of aluminum. Metallurgija 2006, 45, 21–29.

[24] Liapina, T.; Mittemeijer, E.J.; Leineweber, A.; Knapp, M. γ',-Fe4N formation in decomposing ε-Fe3N: A powder diffraction study using synchrotron radiation. Z. FÜR Krist. Suppl. 2006, 23, 449–454. [CrossRef]

[25] Available online: https://www.alliedmarketresearch.com/aluminium-market (accessed on 20 December 2019).

[26] Available online: https://www.grupakety.com/Media/files/PROGNOZA_3.pdf (accessed on 8 February 2019).

[27] Steiner, T.; Mittemeijer, E.J. Alloying element nitride development in ferritic Fe-based materials upon nitriding: A review. J. Mater. Eng. Perform. 2016, 25, 2091–2102. [CrossRef]

[28] Clarke, S.J. Encyclopedia of Materials: Science and Technology; Buschow, J.K.H., Cahn, R.W., Veyssiere, P., Flemings, M.C., Eds.; Elsevier Ltd.: Amsterdam, The Netherlands, 2001.

[29] Farault, G.; Gautier, R.; Baker, C.F.; Bowman, A.; Gregory, D.H. Crystal Chemistry and Electronic Structure of the Metallic Ternary Nitride, SrTiN2. Chem. Mater. 2003, 15, 3922–3929. [CrossRef]

[30] Fromhold, A.T., Jr. Fundamental Theory of the Growth of Thick Oxide Films on Metals. J. Phys. Soc. Jpn. 1980, 48, 2022–2030. [CrossRef]

[31] Roosendal, S.J. Passivation Mechanisms in the Initial Oxidation of Iron by Oxygen and Water Vapor. Ph.D. Thesis, University Utrecht, Utrecht, Netherlands, 1999.

[32] Chemical kinetics. In Reactions of Solids with Gases; Bamford, C.H.; Tipper, C.F.H.; Compton, R.G. (Eds.) Elsevier: Amsterdam, The Netherlands; Oxford, UK; New York, NY, USA; Tokyo, Japan, 1984; Volume 21.

[33] Li, Y.; Wang, L.; Zhang, D.; Shen, L. The effect of surface nanocrystallization on plasma nitriding behaviour of AISI 4140 steel. Appl. Surf. Sci. 2010, 256, 4149–4152. [CrossRef]

[34] Castro Munoz, A.E.; Piedad-Beneitez, A.; Valencia-Alvarado, R.; López-Callejas, R.; Mercado-Cabrera, A.; Pena-Eguiluz, R.; Rodriguez-Mendez, B.G. The Corrosion Enhancement due to Plasma Post-Oxidation Subsequent to Plasma Nitriding of a Steel AISI 4140. Acta Phys. Pol. 2015, 128, 824–827. [CrossRef]

[35] Cao, Y.; Norell, M. Role of Nitrogen Uptake During the Oxidation of 304L and904L Austenitic Stainless Steels. Oxid. Metals 2013, 80, 479–491. [CrossRef]

[36] Yuan, X.; Zhao, Y.; Li, X.; Chen, L. Effects of gas nitriding temperature on the surface properties of a high manganese TWIP steel. Metals 2017, 7, 102. [CrossRef]

[37] Ertl, G.; Huber, M. Interaction of Nitrogen and Oxygen on Iron Surfaces. Z. Fur Phys. Chem. Neue Folge 1980, 119, 97–102. [CrossRef]

[38] Kniep, R. Ternary and quaternary metal nitrides: A new challenge for solid state chemistry. Pure Appl. Chern. 1997, 69, 185–191. [CrossRef]

[39] Steiner, T.; Meka, S.R.; Bischoff, E.; Waldenmaier, T.; Mittemeijer, E.J. Nitriding of ternary Fe–Cr–Mo alloys; role of the Cr/Mo-ratio. Surf. Coat. Technol. 2016, 291, 21–33. [CrossRef]

[40] Tacikowski, J.; Wach, P.; Michalski, J.; Burdyn´ski, K. Separation hardening by heat treatment of nitrided carbon steel. Mater. Eng. 2014, 6, 552–555.

[41] Andrzejewska, E.; Gonzalez-Arrabal, R.; Borsa, D.; Boerma, D.O. Study of the phases of iron–nitride with a stoichiometry near to FeN. Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At. 2006, 249, 838–842. [CrossRef]

[42] Orlik, R.; Ratajski, J.; Suszko, T.; Michalski, J.; Dobrodziej, J.; Gilewicz, A. Precise shaping of phase structure and thickness of nitrided layer on the example of dies for pressure casting of aluminium. Surf. Eng. 2009, 3, 15–20.

[43] Xu, C.H.; Gao, W. Pilling-Bedworth ratio for oxidation of alloys. Mater. Res. Innov. 2000, 3, 231–235. [CrossRef]

[44] Dwivedi, D.; Lepková, K.; Becker, T. Carbon steel corrosion: A review of key surface properties and characterization methods. RSC Adv. 2017, 7, 4580–4610. [CrossRef]

[45] Melchers, R.E. Predicting long-term corrosion of metal alloys in physical infrastructure. NPJ Mater. Degrad. 2019, 3, 1–17. [CrossRef]

[46] Mao, W.; Ma, Y.; Sloof, W.G. Internal Oxidation of Fe–Mn–Cr Steels, Simulations and Experiments. Oxid. Metals 2018, 90, 237–253. [CrossRef]

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COMPANY PROFILE ///

GRAPHITE METALLIZING CORPORATION

SOLVING THE TOUGHEST BEARING PROBLEMS

Pillow blocks. (Courtesy: Graphite Metallizing Corporation)

With more than 150 grades of GRAPHALLOY, a unique graphite/metal alloy, Graphite Metallizing Corporation is uniquely suited to offer submerged or high-temperature products that must function where oil, grease, and plastics fail.

By KENNETH CARTER, Thermal Processing editor

Heavy-industrial machinery is often submitted to harsh, unforgiving environments capable of damaging or destroying equipment and components, as well as a company's bottom line.

With that in mind, it is in a company's best interests to invest in products that can keep equipment performing for a long time.

The experts with Graphite Metallizing Corporation (GMC) have been committed to this goal for more than a hundred years.

The company has done this by developing a method for putting molten metal into graphite to create a new material called GRAPHALLOY.

WHAT IS GRAPHALLOY?

GRAPHALLOY, a graphite/metal alloy, is a proprietary material that has exceptional mechanical, chemical, and tribological properties.

"It's not an easy process; it's actually a foundry process where you impregnate the molten metals into the graphite substrate to make it all the way through; it's a uniform product of graphite and metal," said Eric Ford, vice president of sales and marketing at Graphite Metallizing Corporation. "The graphite makes it self-lubricating, so you don't need any grease or other lubricants. And the metal actually pulls heat away from the shaft, so you don't have any thermal issues. We have grades that can go up to a thousand degrees Fahrenheit in oxygen and about twice that in a non-oxygen environment."

This can become essential for furnaces that operate at a very high temperature, according to Ford. GRAPHALLOY works where traditional bearing materials often fail. It is particularly useful where petroleum lubricants cannot be used, for example, at high temperatures and in submerged applications.

"A lot of times, if you're using grease bearings or solid lube, it can fail because the grease burns out or gets too hot; it seizes the bearings," he said. "That causes a lot of downtime, a lot of maintenance time, and a lot of replacements on those bearings. But with GRAPHALLOY, since it's self-lubricating because of the graphite, it can handle very high temperatures. It will never seize."

VERY TOUGH MATERIAL

Self lubricating GRAPHALLOY withstands high temperatures, performs well under cryogenic conditions, and can survive dry running in pumps, according to Ford. It maintains its integrity even when submerged in hostile liquids such as acids, alkalies, hydrocarbons, black liquor, and natural gas liquids (NGL). GRAPHALLOY can be custom designed for specific application dimensions and tolerances.

"The GRAPHALLOY family of materials consists of many different grades; we have products that we've developed for quench chambers that could be submerged for many, many years," he said. "We also have heat-treat-damper applications that we can handle with GRAPHALLOY, as well as furnace elevators. GRAPHALLOY has quench tank applications where it's worked submerged for over 20 years before being replaced."

Cam followers. (Courtesy: Graphite Metallizing Corporation)

MAKING THE CASE FOR GRAPHALLOY

Recently, a quench tank in a rotary forge shop was using a large shaft with sprockets and chains. The application was submerged and needed a long life between overhauls, but the application required the entire assembly to be split.

GMC supplied standard type 478 pillow blocks with a maximum shaft diameter of six inches, so the shafting had to be slightly reduced. GMC made custom four-bolt, self-aligning, type 478 pillow blocks with the entire assembly split, with perfect halves.

Those original pillow blocks assemblies were sold in 1982 and worked submerged until 1998 when they were shipped back to GMC to be sandblasted, holes tapped, and bushings and bolts replaced. After that, they still ran submerged for more than nine years longer until the customer purchased 12 new pillow blocks.

In another application, GMC was able to save an automotive engine plant more than $100,000 a year by converting its gas-nitriding furnaces to GRAPHALLOY.

Those are just two examples of how GMC's standard and custom designed products can provide lifetime cost savings over conventional bushings and bearings, according to Ford.

A sample of parts made from GRAPHALLOY. (Courtesy: Graphite Metallizing Corporation)

WORKING WITH CUSTOMERS

"When customers come to us with a challenge — which happens every day — they work one-on-one with our engineers," he said. "The first thing we do is make sure they understand what GRAPHALLOY is, and what it can do. We want to make sure they understand the loads it can handle, the speeds, the temperatures — everything — so that it can meet their application, exactly. We don't want them to use it in an application unless it's really going to work."

GMC has a staff of engineers that is always at the ready to speak with customers about their specific applications, according to Ford.

"The other challenge we have is that sometimes people have assumptions of how you use the materials, so, we have to really explain it to them, because it is very different, very unique," he said. "We help them understand how they can use GRAPHALLOY to save themselves time and money. We also make GRAPHALLOY with custom dimensions for customers. If they give us specific information about an application, we'll provide them with a custom bushing solution. We are always interested in discussing new and challenging applications. Sometimes, the customer wants to test GRAPHALLOY in their application, so we provide them with products so they can do some testing and be comfortable with the product. We're seeing that quite a bit as people refurbish, and where they decide they want to save costs."

With many customers bringing their heat treating back in-house in order to have more control over their quality and costs, it becomes even more necessary that GMC work closely with them in order for them to see what GRAPHALLOY can do for them, according to Ford.

"We're also seeing increased investment in existing heat-treat facilities for refurbishing and increasing capacity," he said. "As they expand and they modernize, many times they want to reduce maintenance costs, and that's where GRAPHALLOY products can help."

1913 ORIGINS

The concept of GRAPHALLOY began in 1913 when two engineers developed a method to combine graphite with metal to make electrical contacts for elevators, according to Ford.

And that was a big part of the business until the 1940s, when GMC began to make the product into bushings form and sold to the high-temperature and industrial areas.

"Over the years, Graphite Metallizing developed additional grades of GRAPHALLOY to address new applications," Ford said. "Our engineers have extensive experience with all types of industrial machinery and work with customers to design custom-engineered solutions for their toughest application problems."

Now, GMC, which is ISO 9001/2015 certified, supplies industrial customers worldwide with engineered solutions for severe service applications. The company's corporate headquarters and manufacturing facility is in Yonkers, New York, and its customers include major industrial companies in markets such as oil and gas, power plants, steel, pulp and paper, glass manufacturing, heat treating, metal processing, and food equipment.

LOOKING TO THE FUTURE

And as GMC continues on into its second century, Ford expects GRAPHALLOY to have a significant influence in the aerospace and automotive segments.

"We believe the future continues to be modernization and automation," he said. "The emphasis is going to be on controlling costs with tighter control over intellectual property. And that comes from customers bringing their heat-treat back in-house. We also anticipate tremendous growth in additive manufacturing. These are all areas where GRAPHALLOY products can help to reduce maintenance and other costs."

In the meantime, GMC will continue to demonstrate how GRAPHALLOY can be a tremendous benefit to the heat-treat industry, according to Ford.

"Our philosophy is to provide a quality self-lubricating material to solve really high-temperature issues in the heat-treating process, whether that's furnaces, cart wheels, dampers, quench tanks, or other problem areas," he said.

MORE INFO www.graphalloy.com

ADVERTISER INDEX ///

TOM MORRISON /// FURNACES NORTH AMERICA SHOW PRODUCER

"We're very excited about the opportunity to build an incredible experience."

When did you make the decision to take FNA virtual?

Our Executive Committee has been meeting weekly since April when COVID-19 really started to take shape. We were tracking trends because we knew that Furnaces North America is our marquee event. It draws about 1,800 people, so we wanted to make sure we made the right decisions. We needed to make sure we did the right thing for the safety of the people coming to that meeting — both for exhibitors and attendees. We monitored it, and we really tried to do everything possible to meet live because everybody loves that in-person connection.

In early July, the Board met and decided to move the meeting to a virtual environment, and we're excited about this. Never in the history of heat treating has anyone experienced a digital event like this.

Typically, only about 1 percent of the industry attends a heat-treating trade show. Now, one of our biggest benefits is that we're going to be able to reach out and touch, through every computer screen, 100 percent of the industry with a trade show and virtual sessions. We're very excited about the opportunity to build an incredible experience; giving people a chance to receive relevant content, learn about industry trends, see product demonstrations, and take in the latest in technology that suppliers are bringing to the marketplace — all from your computer.

Was it difficult to make the shift?

It was. Mainly because we actually surveyed every attendee that ever came to FNA, plus the MTI members. It'd be easy if it was 90 percent of the people saying they would attend a live event or 90 percent saying they would want to do a virtual event because of COVID, but it wasn't that easy; 60 percent were one way and 40 percent the other way.

What you don't want is to do a big trade show for exhibitors, and they spend a lot of money to set up and be there with the equipment, and then you have a lackluster crowd because of COVID.

Were some of the events easier than others to transplant to a virtual environment?

If you're only hosting conference sessions, it's easy to do, but when you want to implement a networking environment, it becomes a fairly complicated element.

What steps have you taken to make the experiences as personal as possible?

There are three things people look for in a conference like this: They're looking to get connected with other attendees. They're looking to get all the good content they can by interacting with a speaker, and they're looking to see the best technology they can from an equipment standpoint. Visitors are going to be able to search by category or search by keyword. You can type in "calibration" in the exhibit hall area, and every company that offers calibration — whether it's equipment or service — is going to come up.

You can click on booths. The booths you're going to see look like the booths in a live scenario.

In that booth, you're going to be able to look at technical and marketing documents. You're going to be able to click on product demonstrations the exhibitors would have performed via video, but here's the fun thing: You're going to be able to click on an area called "booth staff" that will list up to 10 people in the booth area. You'll be able to see them online, waiting for you. You can click on that person, and you can invite them to chat, do an audio call, or even a video call online.

There are going to be four live conference sessions and 35 technical sessions that have been pre-recorded by the session presenters. It's tough to present to your audience while questions are put in the chat box because you get distracted, and you end up answering questions instead of presenting. Since presentations are pre-recorded, during the presentation, you can ask the presenter questions as he's presenting. The presenter's going to be freed up to answer those questions right away. It's a very cool experience, and we're excited to give attendees the chance to connect with the experts.

In the Networking Lounge, you'll find people chatting about issues. There'll be an exhibitor chat box. There'll be a session chat box and then, the general FNA chat box. You can chat with the entire group, or you can invite up to 10 people into a group video chat. You'll be able to meet and greet people just like you would in person.

What can attendees expect that might not have been possible in an in-person format?

We've got a special "Bring Your Team" package, where the price for the first two registered is $199, then everybody after that's only $49. We're trying to take the financial obstacle out of the equation.

Can people register up until the time of the show?

Absolutely, although the "Bring Your Team" pricing ends September 15.

What have you learned from this experience that you might use in planning the next FNA?

The No. 1 thing I've learned is to be prepared for anything, and have a Plan B ready to go and be able to make quick decisions — sometimes, with not all of the information. Furnaces North America is a very systematic operation. It's done the same way every year with some changes in order to add some excitement to it, but when COVID came along, it taught us that we need to be prepared for the thing we can't see, so that when it happens, we have a plan in place to make those changes.

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