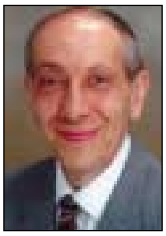
About the columnist . . .

Daniel H. Herring is president of The Herring Group Inc., Elmhurst, Ill., a business specializing in practical solutions to problems facing the heat treating and sintering industries (Web: www. heat-treat-doctor.com).



Dan Herring has spent more than 25 years working for furnace equipment manufacturers in a variety of roles, including senior management and new business development. Now an independent entrepreneur, Dan lectures, writes, teaches, and consults. A frequent speaker at local, national, and international conferences, he is dedicated to advancing the state of the art in thermal processing. He has published more than 100 technical papers, written three books, and contributes to Heat Treating Progress *and other industry publications.*

Dan's credentials include his appointment as a research associate professor at the Thermal Processing Technology Center, Illinois Institute of Technology, Chicago. He also serves on the ASM Heat Treating Society Board and is active on several HTS Committees.

Generic and practical information presented here is not intended to replace or supplement federal, state, and local codes, government standards, insurance requirements, company policies and procedures, or common sense. In addition, all equipment manufacturers' instructions and operating and maintenance manuals should always be thoroughly read and followed. Further, personnel training should be provided unequivocally to everyone who will be associated with operating such equipment.

What to Do About Metal Dusting

Within a heat treating furnace war is being waged between the life of internal components and the destructive forces of temperature and atmosphere. The weapons of the enemy are numerous and include hot gaseous corrosion in the form of carburization, oxidation, sulfidation, and nitridation. At stake for the heat treater is the cost of lost production and the nuisance of downtime for maintenance.

To withstand these attacks, heat-resistant iron-nickel-chromium alloys are chosen for components such as radiant tubes, fans, heating elements, roller rails and rollers, chain guides, and atmosphere inlet tubes. These alloys provide adequate strength if operated within their temperature limits. (Evaluate "1% creep in 10,000 hours" data to help determine which alloy will perform best at a given temperature.)

Although we tend to focus on resisting the effects of high temperature, there is a silent killer that stalks furnace parts in the intermediate temperature range of 450 to 800°C (840 to 1470°F). At these temperatures, materials exposed to carbonaceous atmospheres are particularly susceptible to a phenomenon called "metal dusting," or catastrophic carburization, which causes premature failures by rapidly "wearing away" the surface of the alloy until mechanical failure occurs.

We seldom think about this intermediate temperature range, because our alloys are very strong at low temperatures and most heat treating processes take place at elevated temperatures. However, exposure to intermediate temperatures can occur in transition areas, such as where alloy parts penetrate insulating refractories, or where there are temperature differentials, such as the underside of inner doors or where chain guides exit the heating chamber.

Since these heat-resistant alloy parts are often the most expensive furnace components, heat treaters should have an understanding of how they can be attacked by metal dusting, and what can be done to extend their life by minimizing or preventing it.

What is metal dusting?

Metal dusting is an erosion process in which a metallic component disintegrates into a dust of fine metal and metal oxide particles mixed with carbon.

Generally, metal dusting occurs in a localized area, and how rapidly the disintegration progresses is a function of temperature, the composition of the atmosphere and its carbon potential, and the material. Other significant factors include the geometry of the system, reaction kinetics, diffusivities of alloy components, the specific-volume ratio of new and old phases, and the ultimate plastic strain.

Metal dusting usually manifests itself as pits or grooves on the surface, or as an overall surface attack in which metal thickness can be literally reduced to that of foil.

Examples: A plate made of Alloy 330 (UNS N08330) was mounted underneath a refractory-lined inner door on an integral quench furnace. The atmosphere passed underneath the door and into the quench vestibule. Plate thickness was reduced from 12.5 mm (0.5 in.) to less than 0.75 mm (0.03

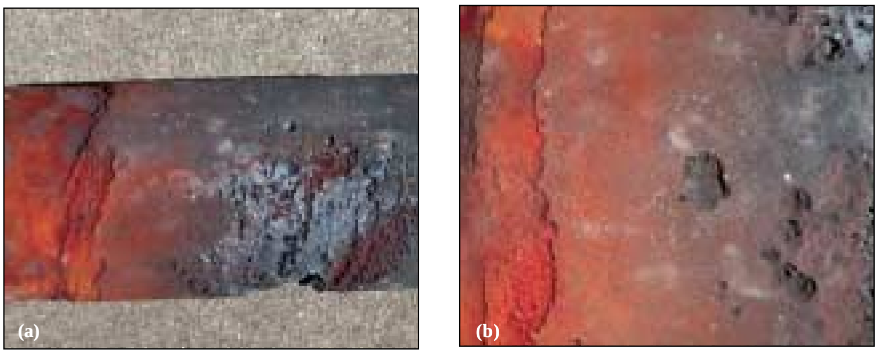


Fig. 1 — (a) Metal dusting is evident on this section of a 150 mm (6 in.) in diameter radiant tube in an area inside the brickwork of a rotary retort furnace. The material is HT alloy (UNS J94605), a cast Fe-Ni-Cr alloy having this composition: 0.35–0.75 C, 15–19 Cr, 33–37 Ni, bal. Fe. (b) Close-up shows the devastating effect of metal dusting (or catastrophic carburization). Sample courtesy BorgWarner Morse TEC Inc., Ithaca, N.Y.

in.) in a little over two months. Composition of the wrought heat-resistant alloy: 0.08 C max, 17–20 Cr, 34–37 Ni, bal. Fe.

Photomacrographs of metal dusting of a cast HT alloy (UNS J94605) radiant tube are shown in Fig. 1. The alloy's composition: 0.35–0.75 C, 15–19 Cr, 33–37 Ni, bal. Fe.

How does it occur?

In general, metal dusting of ferrous alloys proceeds via the formation and subsequent disintegration of metastable carbide. The first step in the process is adsorption of the gaseous phase on the surface of the metal; the more reactive this phase, the easier it decomposes or is catalytically decomposed (in the case of iron) on the surface. This step is followed by diffusion of carbon atoms from the surface into the bulk metal.

As a result, there is a continuous buildup of carbon within the surface layer. As this layer becomes saturated with carbon, a stable carbide, metastable carbide, or an activated carbide complex forms which then grows until it reaches a state of thermodynamic instability, at which point it rapidly breaks down into the metal plus free carbon.

It's at this stage that the metal disintegrates to a powder as the result of plastic deformation and subsequent fracture in the near-surface layer. The process is controlled by internal stresses due to phase transformation; in other words, competition between stress generation and relaxation exceeds the ultimate strength in this near-surface layer and fracture occurs.

High-nickel alloys: By contrast, in high-nickel alloys like HT, the phenomenon occurs slower (but does not stop) since the disintegration leads to larger metal particles which are less active catalysts for carbon deposition than the fine iron particles that form with ferrous metals. Therefore, the mass gain from carbon depositing onto high-nickel alloys is much lower. Also, the decomposition of high-nickel alloys occurs by graphitization and not via unstable carbides.

What is happening?

The first stage of metal dusting occurs when carbon monoxide decomposes to carbon dioxide and carbon on the surface of the alloy:

$$2CO \rightarrow CO_2 + C$$

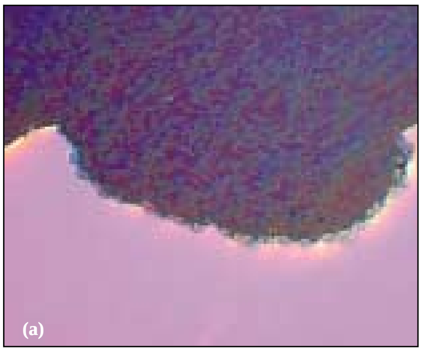
This reaction tends to proceed at temperatures between 315 and 730°C (600 and 1350°F); that is, in approximately the same temperature range at which metal dusting occurs.

In the second stage of metal dusting of ferrous metals, iron carbide particles form and grow:

$$3Fe + C \rightarrow Fe_3C$$

These precipitates then deteriorate, followed by the rapid disintegration of the bulk metal. It has been theorized that cementite in the iron-carbon system is metastable up to a particular concentration and precipitate size, after which it reverts to iron plus carbon. After this occurs, reactivity may be traced to the evolution of the heat of dissociation of the iron carbide, but its effect is small.

Example: A metallographic investigation of the cast HT alloy radiant tube (Fig. 1) was conducted. Photomicrographs at 100X and 1000X of the inside and outside diameter surfaces in the metal-dusted area (Figures 2 and 3, respectively) reveal evidence of massive carbides. These carbides formed by the reaction of carbon with iron and chromium, depleting the matrix in regions adjacent to the carbides. Grain detachment and subsequent failure by erosion then occurred.



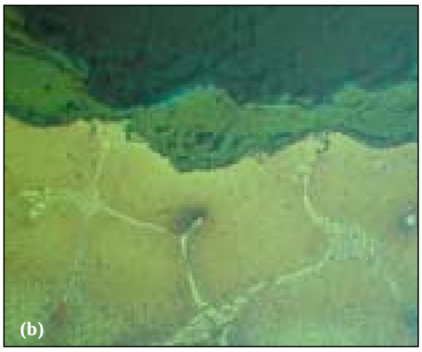


Fig. 2 — (a) Surface pit resulting from severe metal dusting and oxidation on the outside diameter of the cast HT alloy radiant tube. Unetched, differential interference contrast (DIC). 100X. (b) The surface pit at 1000X. The austenite matrix underneath the surface oxidation contains a complex network of (eutectic) carbide (due to the high carbon content). Note that the larger patches of primary carbide have a lamellar structure. General precipitation of fine carbide has occurred. Kallings II, DIC. Photomicrographs courtesy Aston Metallurgical Services Co. Inc., Wheeling, Ill.

How can I avoid it?

What can be done to minimize metal dusting of alloy furnace components? First, determine which areas of the furnace experience intermediate temperatures, and then establish an alloy inspection schedule.

Next, ensure that areas where alloy components transition or pass through refractories are well-insulated. This will make it more difficult for the furnace atmosphere to penetrate into areas that "see" intermediate temperatures. (Failure to do this is a major mistake that often is made during repair or rebricking of an atmosphere furnace.)

Operating practices for heat treating furnaces should also be reviewed. Idling furnaces at reduced temperatures, with continuous endothermic atmosphere flow, over long weekends or other periods of inactivity should be reconsidered if metal dusting is the primary mode of alloy failure. Cycling furnace temperature is never a good idea, and it will accelerate the metal dusting process.

Alloying: Finally, take a close look at the alloys selected for specific applications. It is of little benefit to use less expensive materials if they need to be replaced more often. Suppliers have a great deal of information about metal dusting and other failure mechanisms, and can offer guidelines for alloy selection. For example, the addition of silicon can have a beneficial effect on resistance to metal dusting. A rule of thumb states that metal dusting will be reduced if the alloy can satisfy this criterion: $\%Cr + 2 \times \%Si > 24\%$.

Note, too, that sulfur either as an additive in the material or present from hydrogen sulfide gas can inhibit or even prevent metal dusting by sup-

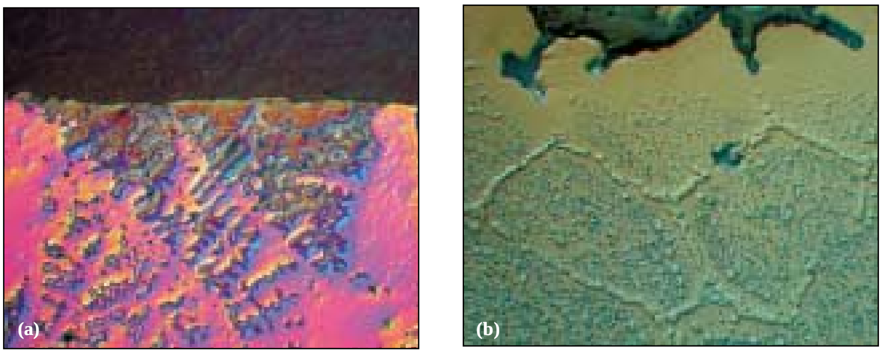


Fig. 3 — (a) Surface and subsurface attack on the inside diameter of the cast HT alloy radiant tube. Unetched, DIC. 100X. Dendritic structure is clearly visible. (b) Image at 1000X of the right side of the specimen. The (eutectic) carbide particles have agglomerated and formed continuous networks. Coarsening of secondary carbide has also occurred. Kallings II, DIC. Photomicrographs courtesy Aston Metallurgical Services Co. Inc., Wheeling, Ill.

pressing the nucleation of graphite. Unfortunately, sulfur also is extremely harmful to nickel-bearing alloys due to the formation of a low-melting-point eutectic.

Coating: Another approach to avoiding metal dusting is to use a coating, especially in transition areas. Note that surface oxides, which generally take the form of a chromium-rich duplex layer in the intermediate temperature range, should be effective, but they are reduced by the furnace atmosphere. Ceramic or "frit" coatings, or aluminum diffusion coatings are effective. However, metal dusting still can occur at defects in the coating, resulting in pitting.

In conclusion, a proactive approach is necessary to help the alloy components inside heat treating furnaces fight this destructive enemy. **HTP**

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