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Vacuum—another atmosphere?

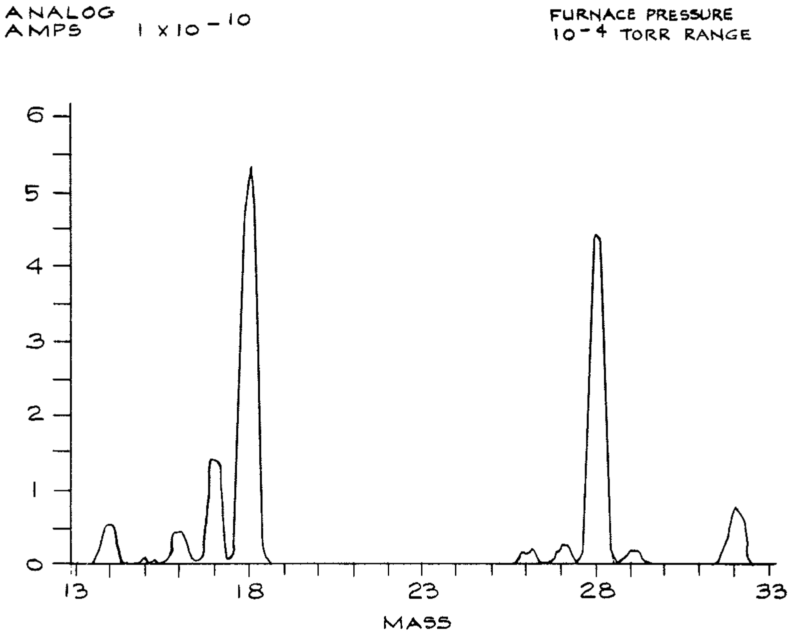
The third installment of our series on the practical aspects of vacuum heat treating explores the oxidizing and reducing aspects of vacuum and how the heat treater can cope with them.

by WILLIAM R. JONES

Old hands in our industry have spoken of vacuum heat treating in terms of other neutral atmospheres, such as nitrogen gas, or even quasi-neutral gases such as exothermic gas from a producer generator. But is vacuum a neutral atmosphere, slightly reducing, or oxidizing? And what about reported alloy depletion and those strange accumulations and deposits the vacuum furnace seems to manufacture?

Absolute vacuum is for all practical purposes unachievable on earth, where pressure levels in the 10^{-13} torr range would be required. Apparently near-absolute vacuum does exist in outer space where these pressures exist and the distance between molecules is on the order of a mile. Today, a vacuum-tight (leak rate less than 5 microns Hg/hour) and adequately diffusion-pumped high-vacuum furnace will operate in the 10^{-5} to 10^{-4} torr pressure range without any difficulty. **Fig. 1** shows the residual gas analyzer (RGA) spectrum for such a furnace when it is empty, cold, and within 15 minutes of vacuum pump down from air. The typical residual air spectrum can be seen with peaks at mass 14/mass 28 nitrogen and mass 32 oxygen. However, the majority of peaks are at mass 16, 17, and 18—the classic water vapor data response. Water vapor is always the predominant residual gas in the industrial vacuum furnace. With continued vacuum pumping for another four hours (not practical in production) while the furnace is cold, the total pressure will fall, particularly the air peaks, but water vapor will dominate to an even greater proportion **(Fig. 2)**.

Fig. 1: RGA data—initial pumpdown, furnace cold



In production operations, one normally pumps down the furnace and turns on the power to the heating elements (either automatically or manually) as soon as the pressure falls below 1 x 10^{-3} torr, one micron Hg. This is usually within 10 minutes of work loading and closing of the furnace door. The residual gas data are difficult to obtain in this poor pressure range and rapidly changing condition, but the data indicate an air spectrum rich in water vapor and complete with solvent peaks such as trichlorethylene and hydrocarbon lubricants or binder peaks as a result of evaporation from the workload, a complex spectrum. This situation continues from ambient temperature to approximately 1200°F and is the classic heavy out-gassing range. Above 1200°F, the water vapor molecules start to dissociate, starting a chain reaction of events. Therefore, in the low temperature range below 1200°F the vacuum furnace can be judged as *slightly oxidizing*. This can be noted when tempering a tool steel like D2 **(Note 1)** which may require a double temper at 950 to 975°F for

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Atmosphere?

Fig. 2: RGA data, prolonged vacuum pumping, furnace cold

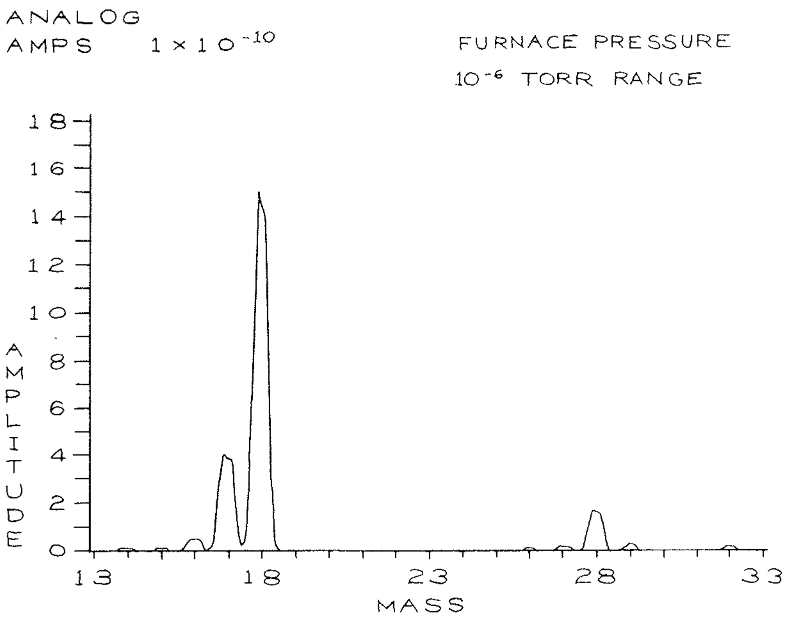
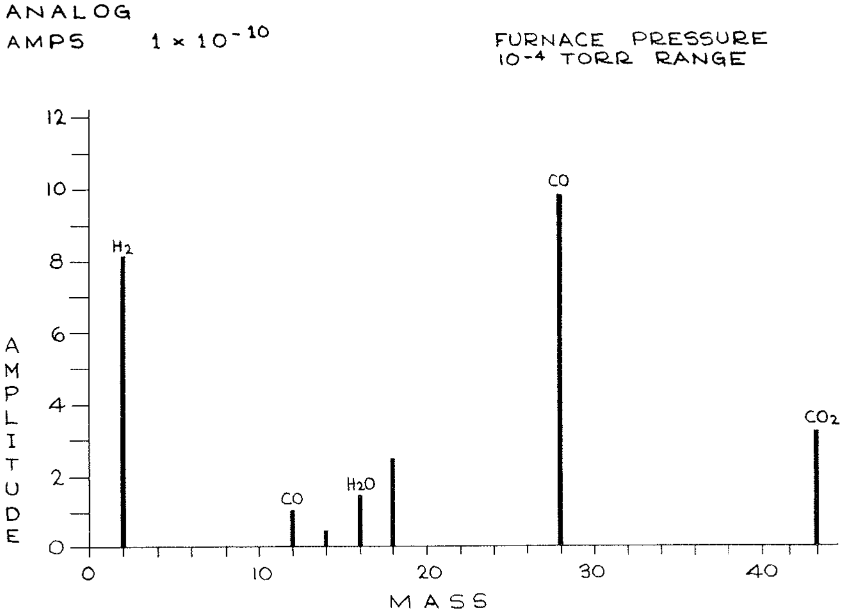


Fig. 3: RGA data, furnace hot, 1950°F



two hours (RC 58-60) or in age hardening a stainless steel like 17-4 pH (**Note 2**) to condition H1075, which requires a four-hour hold at 1075°F. An up-to-date vacuum furnace can keep these parts clean, but a properly conditioned furnace is essential, and the work must be thoroughly degreased and clean; otherwise, oxidized, discolored parts will result.

Above 1200°F, the vacuum atmosphere starts to change dramatically. **Fig. 3** shows typical RGA data at a common temperature, 1950°F, for brazing and heat treating of many materials like stainless steel, type 304.

The ever-present water vapor peaks remain, but mass 32 oxygen is absent. At this temperature the majority of oxygen is catalytically converted to form carbon monoxide mass 28 and carbon dioxide mass 44. This is carried out by residual hydrocarbons (product machining lubricants or vacuum pump oil) in the furnace or carbon/graphite furnace components reacting with the remaining oxygen. (An all-metal radiation shielded hot zone will not prevent this catalytic reaction from occurring; it will be the subject of a subsequent article).

The ever-present water vapor molecule continues to dissociate into hydrogen and oxygen. This oxygen adds to the above reaction, but hydrogen remains. At temperatures above 1800°F and continuing to 3000°F, this RGA pattern is dominant. The vacuum furnace in this temperature range is therefore *slightly reducing* because of the hydrogen and carbon monoxide residuals.

Reinforcing this situation is the metal-metal oxide equilibrium data as derived by W. H. Chang and noted by Bredzs and Tennenhouse (**Fig. 4**). Looking at the curve for the popular chrome oxide (Cr_2O_3), at temperatures below 1000°F, a vacuum level deeper than 10^{-4} torr (.1 micron Hg) is necessary for reduction of this oxide, and at this temperature and a pressure of 10^{-3} torr (1 micron Hg) or poorer, oxidation will occur. At 1950°F the circumstances are very different. Note that this curve indicates it is possible to operate at nearly 500 microns Hg before oxidation occurs. The writer's experience indicates that one should not expect a bright product of a high chrome alloy above 25 microns Hg, even at 1950°F. Often alloys contain other materials such as titanium or aluminum, and traces of these elements form oxides like TiO or AL_2O_3 that are far more difficult to reduce, even at these elevated temperature conditions. The metal-metal oxide curves further support this view.

A properly operating vacuum furnace has the best industrial atmosphere available to the heat treater today. This is due to the sealed vacuum chamber (tighter than even the tightest atmospheric furnace), the continuous purging or pumping of the vacuum system, and the inherent purity derived from reduced-pressure vacuum operation.

High purity argon, Grade 5, from Airco, has a stated total impurity level of 10 ppm (**Note 3**); 10 ppm calculates to 7.5 x 10^{-3} torr (7.5 microns Hg). This could be acceptable in terms of direct comparison to

Fig. 4: Metal-metal oxide diagram

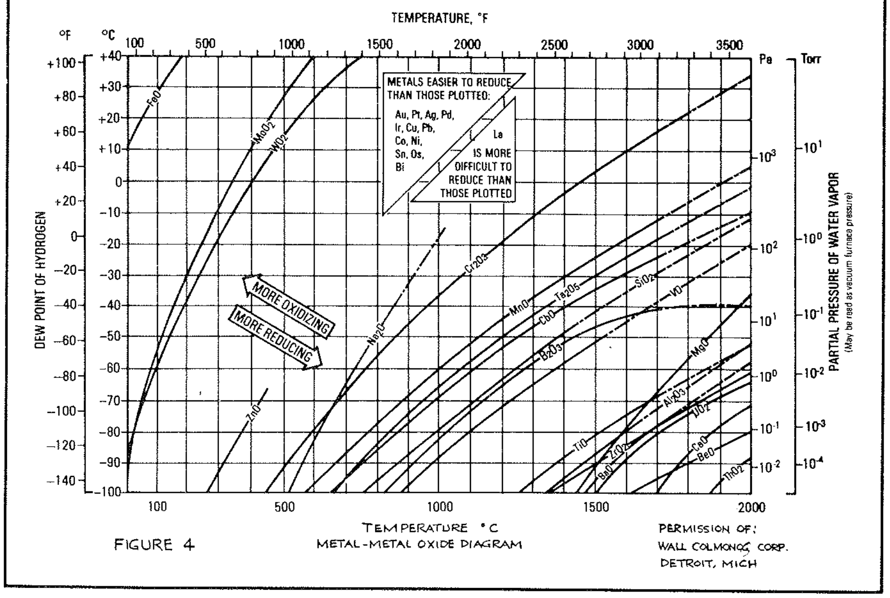


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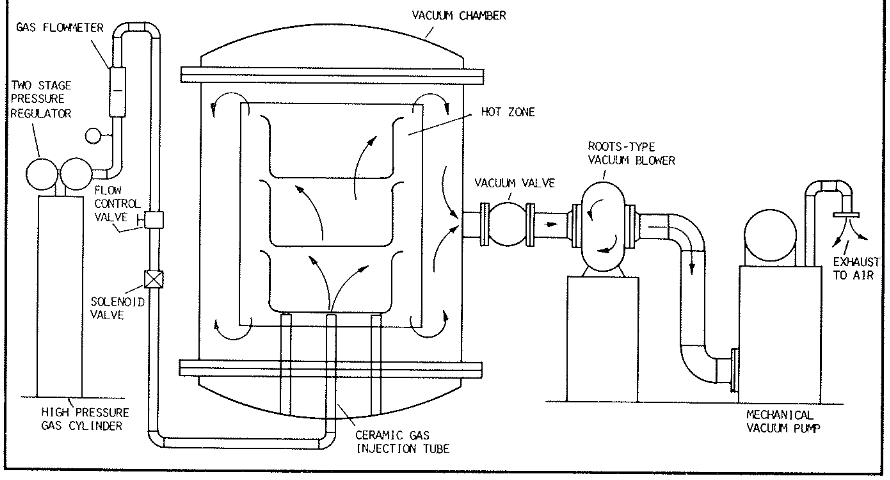
Fig. 5: Gas injection for a vacuum furnace



vacuum operation, but total furnace atmosphere purity is drastically altered by leaks and adulterations from the product, that is, oil, water vapor, and air contamination, all of which must be purged out of the heating chamber. Even at high purge rates these impurities mix and are difficult to sweep out of a retort. Vacuum is definitely the better alternative in this comparison.

Combining gas injection **(Fig. 5)** and vacuum technology offers additional advantages. This is a way to shift the vacuum atmosphere to carry out a specific reaction. So-called "vacuum carburizing" uses this technique, in which methane gas is pulsed into the hot zone to shift the vacuum atmosphere drastically to a high carburizing potential for short periods of time.

Hydrogen can also be injected into the hot zone to shift dramatically to a reducing atmosphere. With proper hot-zone construction, oxygen or air can be pumped through the furnace as an oxidizing agent, particularly at low temperatures to "burn off" binder or other contaminants that often are troublesome at high process temperatures. Certain electronic component purification and sealing applications are feasible with this technique.

A significant aspect of gas injection, often referred to as partial-pressure operation, is that it entails injecting gas directly into the hot zone and sweeping contaminating products into the vacuum chamber, out into the vacuum pumping system, and finally to the atmospheric vent. Installing a properly calibrated flowmeter in series with the gas injection line to monitor gas flow rates is far more important than operating pressure. This way, hot-zone volume calculations as compared to flow rates can be worked out in cfh, and purge rates determined for particular processes more in line with experience with sealed retorts and atmospheric furnaces, i.e., five to 10 volume changes per hour. A major improvement over static vacuum is the high throughput of the vacuum pumps when operating at vacuum levels between 1 and 10 torr, allowing rapid and continuous pump-out and purging of the furnace hot zone and providing a very high purity furnace atmosphere. Using argon as an injection gas, it is possible to process sensitive alloys of titanium without alpha case development, even at peak gettering temperatures of 1700° to 1800°F with hot zone materials that otherwise may cause product reactions.

Operating with partial pressures in the range of 1 to 10 torr, rather than the currently popular range of .1 torr (100 micron Hg) to 1 torr (1000 microns Hg), is particularly recommended to reduce alloy evaporation, where the product is held at high temperatures in excess of 2100°F for hold times over one hour. This subject will be covered in detail in following articles. **HT**

Note 1	**D-2**	**Tool steel**
	Cr	12. %
	C	1.5
	Mo	1.0
	V	1.0
	Bal.	Iron
Note 2	**17-4 ph**	**Stain. steel**
	Cr	17. %
	Ni	4.0
	Cu	4.0
	Mn	1.0
	Si	1.0
	Cb-Ta	0.4
	C	0.1
	Bal.	Iron
Note 3	**Airco**	**Gd. 5 Argon**
	N_2	4 ppm
	H_2	2
	O_2	1
	H_2O	1
	CO	1
	Bal.	1

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