

Partial Pressure Vacuum Processing - Part I

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This article is based on a presentation at the Furnaces North America '96 Conference, sponsored by Industrial Heating. In the first part of this two-part series on partial pressure processing, techniques for controlling evaporation of base materials and reactive processing are discussed. In Part II, actual applications for production operations will be presented with full process cycles and descriptions.

Vacuum furnace processing of materials has long been established^[1] as a premier way to insure consistency and cleanliness of parts, i.e., oxide free. There are also many other attributes which are beyond the scope of this article. However, operating the furnace in high vacuum^[2] can lead to evaporation of base metal materials, and since the vacuum atmosphere^[3] is more or less neutral, may not produce as reactive an atmosphere for some applications. These issues are discussed in more detail below.

Evaporation

All materials have some vapor pressure, no matter how slight, and will evaporate slowly even at atmospheric pressure. As the pressure is reduced, i.e., rising in altitude from earth or placed into a vacuum chamber, the surrounding air pressure is lowered allowing a greater freedom for molecular evaporation (see Table I).

For example, the boiling point of water is 212°F at atmospheric pressure and sea level. However, if an open container of water is placed into a vacuum chamber and the pressure is reduced to below 10 torr, the water will boil at ambient temperature (70°F). This is tricky to observe, as after the water begins to boil, the temperature of the water drops to the freezing point, 32°F, and soon one has solid ice. The energy to drop the water from 70°F to 32°F comes from the heat of evaporation of water, and this heat is absorbed from the surrounding mass of the chamber internal structure or the wall of the vacuum vessel. If one has a gal-

lon of water in a vacuum furnace chamber and a large vacuum roughing pump (e.g., 300 cfm), a noticeable section of the vacuum chamber will indicate a "freeze up" with noticeable external dew point or frost condition, and the gallon of water will freeze into a solid block of ice.

Metals, like the water in the example above, will evaporate and are dependent on the vacuum level and temperature. It should be noted that the evaporation rate is dependent on temperature as a first order effect and pressure as a second order effect. This can be seen from the following equation for evaporation rate^[2], Q, and the fact that the vapor pressure/temperature relationship is nearly logarithmic:

$$Q \text{ max} = 0.058 P_v \sqrt{\frac{M}{T}}$$

where Q is in g/c² per second, P_v is the vapor pressure in torr, T is in degrees Kelvin, and M is the molecular weight. The point of this observation is that if evaporation occurs, the first solution is to drop the operating temperature, and the second solution is to raise the pressure. However, generally one cannot drop the temperature for specific process reasons, so raising the pressure is usually the only consideration.

In the heat treatment industry, two major occurrences are the evaporation of chrome from stainless steel-based materials in vacuum heat treating, and evaporation of copper from vacuum copper brazing operations (see Fig. 1),

Table I Pressure at Various Altitudes (from Ref. 10)

Altitude (ft)	Pressure (Torr)	Altitude (ft)	Pressure (Torr)	Altitude (ft)	Pressure (Torr)
-1,000	787.87	7,000	586.49	25,000	282.40
-500	773.83	7,500	575.45	27,500	253.00
0	760.00	8,000	564.58	30,000	226.13
500	746.37	8,500	553.88	35,000	179.33
1,000	732.93	9,000	543.34	40,000	141.18
1,500	719.70	9,500	532.97	45,000	111.13
2,000	706.66	10,000	522.75	50,000	87.497
2,500	693.81	11,000	502.80	55,000	68.889
3,000	681.15	12,000	483.48	60,000	54.236
3,500	668.69	13,000	464.76	70,000	33.662
4,000	656.40	14,000	446.63	80,000	21.010
4,500	644.30	15,000	429.08	90,000	13.208
5,000	632.38	17,500	387.65	100,000	8.356
5,500	620.65	20,000	349.53	120,000	3.446
6,000	609.09	22,500	314.51	140,000	1.508
6,500	597.70				

because in both cases operating temperatures in excess of 2050°F (1121°C) are required. From the vapor pressure data in Table II, the equilibrium vapor pressures for these two materials at this temperature are:

Chrome: 10⁻⁴ torr range
Copper: 10⁻³ torr range.

If one is operating a vacuum furnace with a high vacuum diffusion pump,^[4] or another type high vacuum pump, the vacuum level will generally be below these pressures, thus assuring evaporation.

One would believe that simply raising the pressure to above 10⁻³ torr would stop evaporation. However, this is not the case where only the rate of evaporation is reduced. What is generally required is an operating pressure of 1 torr for chrome and 5 torr for copper to prevent noticeable evaporation.

If evaporation is not suspended in

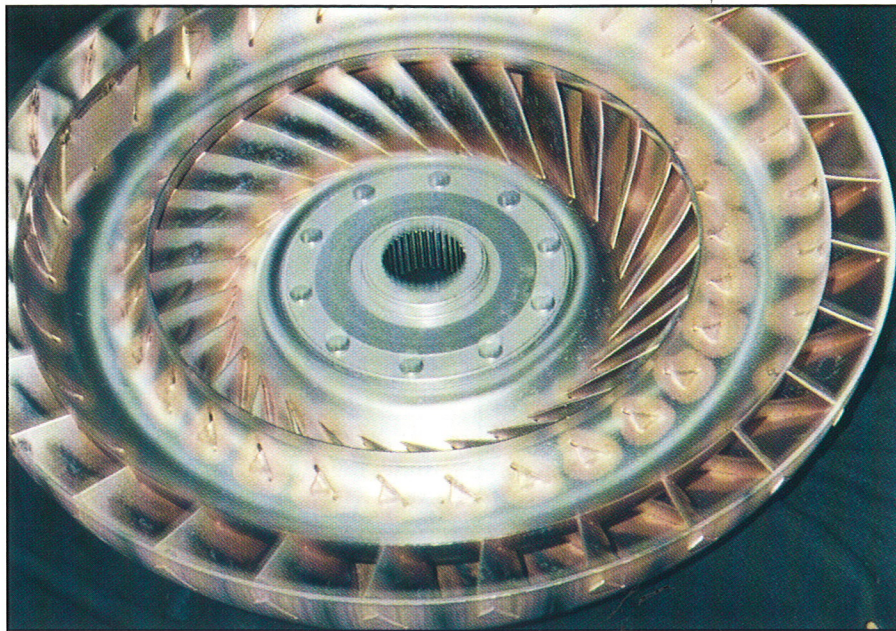


Fig. 1 Copper brazed part assembly processed in partial pressure to prevent evaporation.

Table II Typical Vapor Pressure of the Elements in Torr (from Ref. 11)

Element	Temperature (°C) at which Vapor Pressures are:						
	10 ³	10 ²	10 ¹	1.0	10 ⁰	10 ⁰	760
Aluminum	889	996	1123	1279	1487	1749	2327
Beryllium	1029	1212	1367	1567	1787	2097	2507
Boron	1239	1355	1489	1648	3030	3460	2527
Cadmium	220	264	321	394	484	611	765
Calcium	528	605	700	817	983	1207	1482
Carbon	2471	2681	2926	3214	3946	4373	4552
Chromium	1090	1205	1342	1504			2222
Cobalt	1494	1649	1833	2056	2380	2720	3097
Copper	1141	1273	1432	1628	1879	2207	2595
Gallium	965	1093	1248	1443	1541	1784	2427
Germanium	1112	1251	1421	1635	1880	2210	2707
Gold	1316	1465	1646	1867	2154	2521	2966
Iron	1310	1447	1602	1783	2039	2360	2727
Lead	625	718	832	975	1167	1417	1737
Magnesium	383	443	515	605	702	909	1126
Manganese	878	980	1103	1251	1505	1792	2097
Mercury	18	48	82	126	184	216	361
Molybdenum	2295	2533	2880	3102	3535	4109	4804
Neodymium	1192	1342	1537	1775	2095	2530	3090
Nickel	1371	1510	1679	1884	2007	2364	2837
Palladium	1405	1566	1759	2000	2280	2780	3167
Phosphorus	160	190	225	265	310	370	431
Platinum	1904	2090	2313	2582	3146	3714	3827
Potassium	161	207	265	338	443	581	779
Rhenium	2790	3060	3400	3810			5630
Rhodium	1971	2149	2358	2607	2880	3392	3877
Selenium	200	235	280	350	430	550	685
Silicon	1223	1343	1585	1670	1888	2083	2477
Silver	936	1047	1184	1353	1575	1865	2212
Sodium	238	291	356	437	548	696	914
Sulfur	66	97	135	183	246	333	444
Tantalum	2820	3074	3370	3740			6027
Tin	1042	1189	1373	1609	1703	1968	2727
Titanium	1384	1546	1742	1965	2180	2480	3127
Uranium	1730	1898	2098	2338			3527
Vanadium	1725	1888	2079	2207	2570	2950	3527
Zinc	292	343	405	487	593	736	907
Zirconium	1816	2001	2212	2459			3577

production operations, the furnace internal hot zone will soon become plated with the evaporating material and do serious damage to heating elements and/or insulation materials. If the furnace hot zone uses multiple lay-

ers of metal heat shields^[5] these will soon be destroyed.

Surface "alloy depletion" effects to the product may also be a major concern under these circumstances. With the superalloys,^[6] such as Inconel 718,

the hold time in the furnace may be an hour or longer. In the case of copper brazing,^[7] if large component assemblies are brazed requiring an hour hold time, a high vacuum operation can well evaporate the copper filler metal and lead to joint failure. The cure is operation of the vacuum furnace either in less than high vacuum or in partial pressure vacuum.

Gas Addition

High vacuum is easily decayed with the introduction of gas from an external source. To prevent evaporation, the popular gas additions are nitrogen or argon. Since argon is totally inert, this is often preferred over nitrogen to avoid nitriding of materials that may contain traces of titanium, tantalum, or other elements that may react and form nitrides. Such is the case with stainless steels like 17-4PH. Argon gas is also preferred over nitrogen, since it is generally available with lower trace impurities. The heavier argon molecule tends to further retard evaporation with respect to nitrogen.

The gas source may be from a high pressure bottle or an in-house large bulk supply. Gas pressure should be reduced to approximately 5 PSIG with a pressure regulator and run through a flowmeter with the final pressure drop and control across a throttle valve (see Fig. 2). Note the gas addition is injected directly into the hot zone to allow proper flow and purging of the hot zone. On introduction of the gas, the vacuum operation will shift from the high vacuum pumping mode to the roughing mode thus shutting down high vacuum pumping. The furnace pressure will be set by the amount of gas flow, in the range of 10 to 200 SCFH, as controlled with the throttle valve and observed by a preferable capacitance manometer vacuum gauge in contrast to a thermal-type vacuum gauge where calibration is seriously shifted by the type of gas.

Reactive Processing

Since vacuum is more or less a neutral atmosphere, often it is desirable to shift the furnace atmosphere to reducing or oxidizing for a specific purpose. The atmosphere can be altered also for carburizing or nitriding, depending on the application and/or other situations that may come to mind.

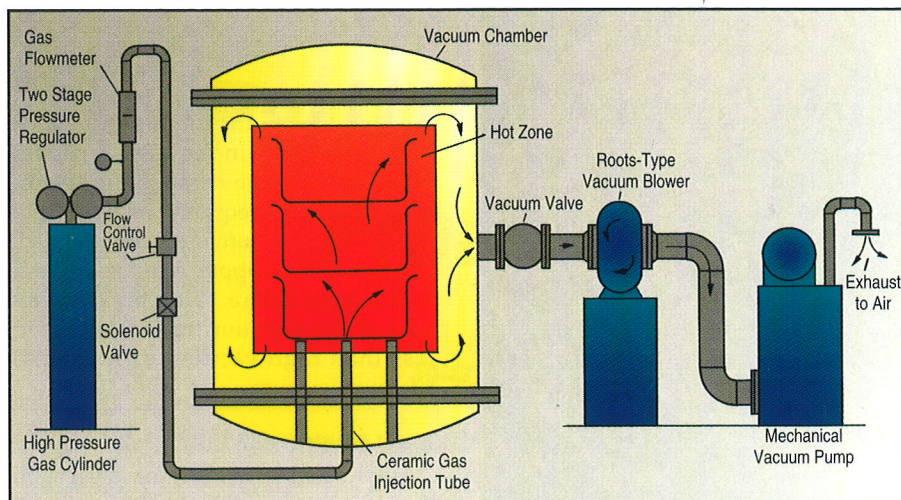


Fig. 2 Gas injection system for a vacuum furnace.

For reducing purposes, that is oxide reduction (such as nickel or chrome oxide to base element), generally hydrogen gas is the preferred choice. Hydrogen gas is, of course, a fire or explosion hazard and addition of this gas should carefully follow the recommendations of the NFPA 86D Standard.^[8] Since oxide reduction generally occurs at high temperature, hydrogen gas is usually not admitted unless the furnace hot zone temperature is in excess of 1400°F and not to a pressure greater than 15 torr, again to stay within the NFPA recommendations. Other gases, such as carbon monoxide, have been utilized, but for obvious hazards are rejected.

For temperatures below 600°F, oxidation reactions can be accomplished by the admittance of air, as air contains a little under 20% oxygen with the balance principally nitrogen and other gases including water vapor. Operations higher than 600°F may cause serious oxidation and damage to hot zone materials such as graphite, molybdenum, or tungsten. However, to burn out certain hydrocarbons, like lubricants or binders from certain materials, this can be a useful preliminary step, followed by full vacuum and other partial pressure gas steps, with obvious precautions to apply.

With the use of diatomic nitrogen (N_2) gas, nitriding can be carried out purposely for materials like titanium or tantalum which will nitride at elevated temperatures and in a nitrogen atmosphere. This is not as effective as using monatomic nitrogen (N) from a dissociated ammonia source, as in standard gas atmospheric nitriding, since the monatomic form is much more

reactive. Dissociated ammonia has been injected as a gas for nitriding, but is not particularly reactive at sub-atmospheric pressure as compared to ambient pressure or higher.

Carburizing gases such as methane, for carbon additions to steels, have been successfully injected in kind and are more fully discussed by Fabian^[6] and by others^[9] active in this field. Since methane and other carburizing gases are flammable and/or explosive, the NFPA 86D rules must be addressed.

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