Case Studies Related to Hydrogen Embrittlement of Fasteners

Part One

扣件氢脆的个案研究 (第一部分)

by Daniel H. Herring

In simplest term, hydrogen embrittlement is a loss of ductility in a metal or alloy caused by the ingress of hydrogen in combination with stress, either applied externally or internally (in the form of residual stress). It is characterized by a loss of ductility and decrease in yield strength of steel and other metals. Of importance to the fastener industry is hydrogen embrittlement of high strength steel resulting from electrochemical surface treatments. It is caused by hydrogen from the process invading the metal lattice and weakening the grain structure over time. Body Centered Cubic structures (BCC) and Hexagonal Close Packed (HCP) structures are more susceptible than Face Centered Cubic structures (FCC), If left unaddressed, hydrogen embrittlement can lead to catastrophic failure of the material.

Baking for Relief of Hydrogen Embrittlement

The most common method to prevent hydrogen embrittlement is through a process called baking (aka bake-out). Baking consists of heating the fasteners to a specified temperature and holding them at temperature generally between 175ºC (350ºF) and 220ºC (430ºF) for a period of 8 to 24 hours *once the parts have reached temperature* (see **Fig 1**). In this writer's eyes, a bake-out of 24 hours after the load has stabilized at temperature is highly recommended.

The process is typically done in convection style industrial ovens, either continuously or on a batch basis. The specific time and temperature necessary are determined by the hardness of the steel **(Fig. 1)** and is also affected by the permeability of the coating. For example, for zinc electroplated fasteners above 39 HRC, common practice is a minimum baking time of 8 to 10 hours at 190º - 220ºC (375º - 430ºF).

It is critical to perform the baking process as soon as possible after plating, otherwise the hydrogen will become fully absorbed into the steel lattice, preventing it from being baked out. Although some specifications call for baking to be performed within 24 hours of plating, it is generally accepted practice to bake within 3 hours of plating, and many manufacturers specify no more than 1 hour. For this reason, many fastener manufacturers use a continuous flow (first in, first out) process so the work in process is minimized and the chance of shipping improperly baked fasteners is reduced.

Some common examples of oven bake-out processes are presented here.

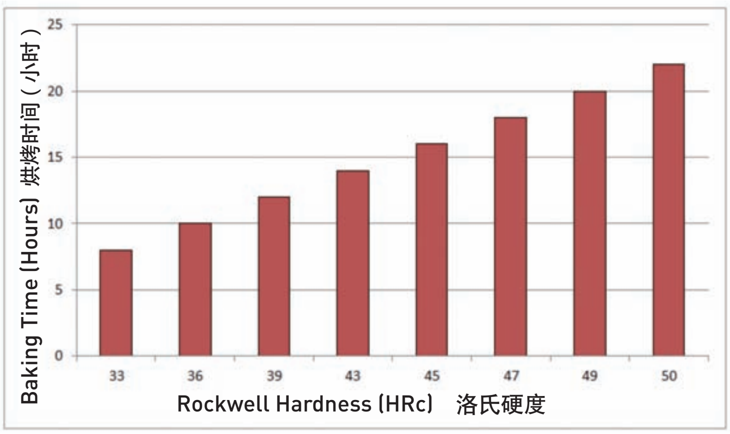

Fig. 1 Recommended minimum hydrogen bake temperatures as a function of hardness (Source: ASTM B850)

图 1 依据硬度函数所建议的最低烘烤温度

用最简单的话形容，氢脆就是金属或合金因为氢结合压力的进入所引起的延展性损失，无论压力是外部施加或内部（残留应力的形态）。它的特点是钢和其他金属的延展性及降伏强度的损失。对扣件产业而言，高强度钢因电化学表面处理产生氢脆，这是个严重的问题。它的成因是氢在处理过程中侵入金属晶格，随著时间的推移削弱晶粒结构。体心立方结构（BCC）和六方密排（HCP）结构比面心立方结构（FCC）更为敏感，如果放任不管，氢脆会导致材料发生灾难性的失效。

以烘烤消除氢脆

防止氢脆最常见的方法是采用一种称为烘烤的程序。烘烤是将扣件加热到给特定的温度，并在扣件达到该温度时，通常将温度保持在175ºC（350ºF）至220ºC（430ºF）之间范围，并且维持 8~24 小时（参照**图 1**）。在笔者的眼里，强烈推荐烘烤的物体在某温度稳定下来之後烘烤 24 小时。

此程序通常是采用对流式的工业炉进行，可连续烘烤或分批烘烤。烘烤所需的时间及温度取决於钢（**图 1**）的硬度，也受到涂层渗透性的影响。例如，对於 39 HRC 以上的镀锌扣件而言，通常的做法是最少 8 至 10 小时的烘烤时间，温度为 190º~220ºC（375º ~ 430ºF）。

电镀後尽快执行烘烤，是非常重要的，否则氢会完全被吸收到钢格里，无法被烘烤排除。虽然一些规范要求烘烤应在电镀後 24 小时之内进行，但一般常态的作法是电镀後 3 小时内即进行烘烤，而许多厂商则规定不超过 1 小时。因此，许多扣件

Case Studies of Hydrogen Embrittlement Relief Using Various Style Bake Ovens

Case Study #1

A conveyorized mesh belt oven **(Fig. 2)** was used to provide embrittlement relief of small screws **(Fig. 3)** used in automotive interiors to hold the interior doors panels in place. The production rate was 1360 kg (3000 lbs.) per hour and the parts were loaded on the 1.2 m (4 ft.) wide conveyor belt at 145 – 195 kg/m^2 (30 - 40 lbs./ft^2), 100 – 150 mm (4 – 6 inches) deep. The baking temperature was 205ºC (400ºF), with a temperature uniformity of ± 5.5ºC (± 10ºF). The parts were brought to temperature in the first zone in approximately 45 minutes, and soaked at temperature for 6 hours. A critical factor was that different types of fasteners needed to be run through the oven and part mixing was not allowed; a cross contamination rate of less than .0001 percent was specified.

Case Study #2

A multiple door batch oven **(Fig. 4)** was designed for hydrogen embrittlement relief of steel rods used in automobiles. The oven has four heating chambers and a load capacity of 1360 kg (3000 lbs.). The steel rods are laid on their sides and slid into the oven on a load rack. The oven has interior dimensions of 2 m (6.5 ft.) wide x 8.5 m (28 ft.) long x 1.8 m (6 ft.) high, a maximum operating temperature of 260ºC (500ºF) and normal operating temperature of 170ºC (430ºF). The heating system features an industrial 215,000 kCal/h (850,000 BTU/hr.) air heat burner. The recirculation system was rated at 340 m^3/min (12,000 ft^3/minute) and utilizes combination airflow to maximize heating rates and temperature uniformity. The air is delivered to each heating zone from both sides near the bottom, and the air passes vertically through the load before returning to the heating system at the top. The batch oven is AMS2750D compliant and achieved a 15-point temperature uniformity of ± 10ºC (± 20ºF) at 170ºC (430ºF). The temperature control was provided via a closed-loop control system utilizing auto-tune.

Case Study #3

A manufacturer of aircraft landing gears needed to simultaneously perform hydrogen embrittlement relief on multiple 1815 kg (4000 lb.) loads. Floor space was at a premium but there was plenty of vertical space available. The solution was to stack multiple bake ovens on top of one another **(Fig 5)**. The interior space required for each heating chamber is 2.4 m (8 ft.) wide x 4.3 m (14 ft.) long x 1.2 m (4 ft.) high, and the three ovens have a total overall height of over 5.8 m (19 ft.). Since the doors are out of reach of operators, they need to open automatically and were pneumatically operated.

Each oven utilizes a 285 m^3/h (10,000 ft^3/minute) recirculation fan powered by a 7.5 kW (10 HP) motor. The heating system for each oven uses a 225,000 kcal/h (900,000 BTU/hr.) burner and has

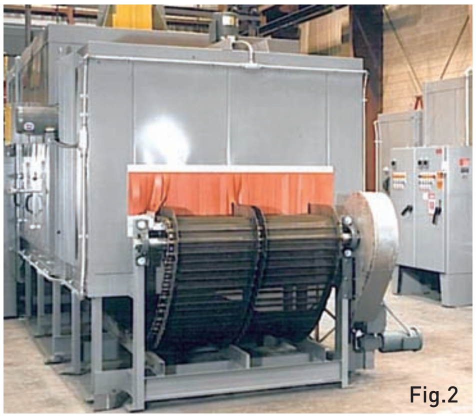

Fig. 2 Mesh belt conveyorized embrittlement relief oven for fasteners
(Courtesy of Wisconsin Oven Corp)

Fig. 3 Automotive Fasteners Were Processed Through a Bake Oven for Embrittlement Relief

图 2 扣件用的输送网带式脆化消除炉

图 3 车用扣件透过烤炉进行脆化消除的处理

厂商采用持续流程（先入先出），使处理程序尽量缩短，并降低烘烤不当的扣件出货的机会。

某些烤炉烘烤的常见范例会在本文中说明。

使用不同型态的烤炉进行氢脆消除的个案研究

个案研究 #1

附有输送网带的烤炉（**图 2**）用於汽车内装中以对固定车内门板的小螺丝（**图 3**）做脆化消除。生产率为每小时 1,360 公斤（3,000 磅），且将零件装载到 1.2 米（4 英尺）宽装的输送带上，装载面积为 145~195 kg/m2 (30~40 lbs./ft2)，深度为 100~150 毫米（4~6 英寸）深。烘焙温度为 205ºC（400ºF），温度均匀性为 ±5.5ºC（±10ºF）。这些零件在第一区域中处於该温度下大约 45 分钟，并以该温度浸泡 6 小时。一个关键因素在於，不同类型的扣件需要通过烤炉；且不允许零件混合；规定须有小於 0.0001%的交叉污染率。

个案研究 #2

多门分批处理烤炉（**图 4**）设计用来对汽车中所使用的不锈钢棒进行氢脆消除。烤炉有四个加热室和 1,360 公斤（3,000 磅）的负载能力。钢棒被平放并以装载架滑入烤炉中。烤炉的内部尺寸为 2 公尺（6.5 英尺）宽 ×8.5 公尺（28 英寸）长 ×1.8 米（6 英尺）高，最高工作温度为 260℃（500ºF）和 170℃的正常工作温度（430ºF）。加热系统采用了工业 215,000 千卡 / 小时（85 万 BTU / 小时）的空气换热刻录机。循环系统之等级为 340 立方米 / 分钟

an independent temperature control system. The parts were baked at 190ºC (375ºF) for 24 hours after chrome plating. A temperature uniformity of +1.7ºC (3ºF), -3.9ºC (7ºF) is maintained inside the heating chamber and the equipment is AMS 2750 (Pyrometry) compliant.

Case Study #4

An aircraft manufacturer required a hydrogen embrittlement relief oven to bake plated parts carried on multiple load carts. A 5-door design **(Fig. 6)** was selected to reduce cost and minimize footprint. 3 doors are located on the front, and 1 on each side. Each of the 5 heating areas accommodates a load cart carrying 180 pounds of parts. The oven interior is 7.6 m (25 ft.) wide x 2.4 m (8 ft.) long x 2.4 m (8 ft.) high.

The baking oven includes an 810 m^3/min (28,500 ft^3/minute) recirculation system, utilizing three recirculation each fans rated at 270 m^3/min (9,500 ft^3/minute) and 7.5 kW (10 HP) each. The oven features a 180 kW electric heating system. The baking temperature ranged from 135ºC (275ºF) to 190ºC (375ºF), and a temperature uniformity of ± 8ºC (±15ºF) was achieved. The equipment conformed to The Boeing Company BAC5621 pyrometry specification. The oven structure was designed to meet seismic requirements.

What Causes Hydrogen Embrittlement?

Although hydrogen embrittlement (aka hydrogen induced cracking or hydrogen attack) is a well-known phenomenon, the exact mechanism by which occurs is a matter of debate despite extensive research. Parts that undergo electrochemical surface treatments such as pickling, phosphate coating, corrosion removal, paint stripping and electroplating are especially susceptible.

During the electroplating process when the electricity is pulling chrome (for example) ions out of solution and reducing them to metal on the fasteners (which is the cathode), it is also electrolyzing the water of solution into H+ and OH-, and drawing those hydrogen ions into the metal. A metallurgical interaction begins to occur between atomic hydrogen and the crystallographic structure of the steel. The hydrogen, in atomic form, will enter and diffuse through the surface of the steel. When a high strength fastener experiencing embrittlement is put under tensile load from tightening, the stress causes atomic hydrogen within the steel

Fig. 4 Batch style oven with multiple doors (Courtesy of Wisconsin Oven Corp)

Fig. 5 Three hydrogen embrittlement relief bake ovens stacked to conserve floor space (Courtesy of Wisconsin Oven Corp)

图 4 多门的分批式烤炉

图 5 三具氢脆消除烤炉堆叠，以节省地面空间

（12,000 立方英尺 / 分钟），利用组合气流使加热速度和温度的均匀性达到最大。空气从底部附近的两侧传递到每个加热区，且空气返回到加热系统的顶部之前垂直穿过装载的物件。此批量处理烤炉符合 AMS2750D 标准，并且加热到 170℃（430ºF）时达到 ±10℃（±20ºF）的 15 点温度均匀度。温度控制是透过自动调谐的封闭回路控制系统来达成。

个案研究 #3

某飞机起落架制造商需要同时对於总重 1,815 公斤的（4,000 磅）零件进行氢脆消除。地面空间非常有限，但有大量的垂直空间可用。解决的办法是将多个烤炉堆叠起来（**图 5**）。各加热室所需的内部空间是 2.4 公尺（8 英尺）宽 ×4.3 公尺（14 英尺）长 ×1.2 公尺（4 英尺）高，且三座炉具总堆叠高度超过 5.8 公尺（19 英尺）。由於作业人员无法触及烤炉的门，这些门需要自动打开并以气动方式操作。

每具烤炉采用 7.5 千瓦（10 马力）马达发动的 285 立方米 / 小时（10,000 立方英尺 / 分钟）循环风扇。每具烤炉的加热系统使用 225,000 千卡 / 小时（90 万 BTU / 小时）的燃烧器，并具有独立的温度控制系统。零件在被镀铬後以 190ºC（375ºF）的温度烘烤 24 小时。加热室内部维持 +1.7ºC（3ºF），-3.9ºC（12ºF）的温度均匀性，且设备符合 AMS2750（测温）规范。

个案研究 #4

某飞机制造商需要使用氢脆消除烤炉烘烤多具推车装载的电镀零件。该制造商选用 5 门（**图 6**）的设计，以降低成本和减少排放量。 3 道门位於正面，每侧各有一道门。5 个加热区均可容纳承载 180 磅零件的推车。烤箱内部为 7.6 米（25 英尺）宽 x 2.4 英寸米（8 英尺）长 X 2.4 英寸米（8 英尺）高。

烤箱包含一套 810 立方公尺 / 分钟（约 28,500 英尺 3 / 分钟）的再循环系统，并使用三具额定为 270 立方公尺 / 分钟（9500 立方英尺 / 分钟）和 7.5 千瓦（10 马力）的风扇。烤箱配有 180 千瓦的电加热系统。烘焙温度的范围，介於 135℃（275ºF）至 190ºC（375ºF）之间，且温度均匀性达到 ±8ºC（±15ºF）。该设备符合波音公司 BAC5621 测温规范。烘炉结构的设计符合抗震规定。

氢脆的成因为何？

虽然氢脆（即氢导致开裂或氢侵蚀）是一个众所周知的现象，其发生的确切机制，尽管进行了广泛研究，仍是一个争论的课题。经过酸洗、磷酸盐涂层、腐蚀除去、脱漆和电镀等电化学表面处理的零件极易发生此问题。

Fig. 6 Multi-door batch style oven for hydrogen stress relief (Courtesy of Wisconsin Oven Corp)

图 6 氢应力消除用之多门分批式烤炉

to migrate to the location of greatest stress (i.e., at the first engaged thread or under the head of a screw). As increasingly higher concentrations of hydrogen collect at this location, the steel gradually becomes brittle. Eventually, the concentration of stress and hydrogen causes microcracks **(Fig. 7)**, which continue to grow as hydrogen moves to follow the tip of the progressing crack, until the fastener fails. As a result, the metal will break or fracture at a greatly reduced load or stress than otherwise indicated. It is this lower breaking strength that makes hydrogen embrittlement so destructive. Unfortunately for fastener manufacturers, as the strength of the steel goes up, so does its susceptibility to hydrogen embrittlement.

Even a small amount of hydrogen can cause embrittlement. Hydrogen levels as low as .0001 percent by weight will cause embrittlement in certain plating applications. Such low levels of hydrogen cause embrittlement through the concentration of the hydrogen at areas of stress in the steel.

How is Hydrogen Embrittlement Detected?

Slow bend tests and tension tests will detect hydrogen embrittlement by revealing the decrease in ductility. Notched–impact tests cannot always detect the phenomenon.

The methods most often used to test threaded fasteners are described in ASTM F606, ASTM F519 and ISO 15330. Of these, ASTM F606 is the most practical for fastener manufacturers and the most often employed, as it can be applied to large numbers of samples from each lot. For case-hardened fasteners the more applicable procedure is ASME B18.6.3, Section 4.11.5. These are sustained load tests, incorporated as a quality assurance measure for testing high strength fasteners after plating. They consist of applying a specified static load for a fixed period of time, from 24 to 200 hours, to test for failure. The basis for these tests is a slow increase of the applied load until rupture of the sample, thus incorporating a time component in the test.

Important Considerations for Hydrogen Embrittlement Relief Baking

Soak Time: Since the fasteners must be brought to temperature and held there for a specified "soak" time to achieve a proper bake, it is important that sufficient time is allowed for heat-up before soaking begins. This requires heating tests on the fasteners to determine how long is required to heat them. The required bake time is then added to this to determine the total heating time.

Temperature Uniformity: For a proper bake, the part temperature must be held within roughly ± 8ºC (± 15ºF) to ± 10ºC (± 20ºF) of the specified bake temperature for the entire period of baking time. It is important, therefore, that the bake oven has the capability to

在电力将（例如）铬离子从溶液抽出，并将其还原到扣件的金属上（即阴极）的电镀过程当中，也会将溶液的水电解成 H + 和 OH-，并将氢离子抽入金属。冶金的相互作用开始在原子氢与钢材的晶体结构之间发生。原子形态的氢，将会透过钢的表面进入并扩散。当高强度的扣件遭遇脆化且因为紧固而处於拉伸的负载，应力会导致钢内的氢原子迁移到最大应力的位置（即在第一接合螺线或螺丝顶部的下方）。当浓度越来越高的氢集合在这此位置时，钢逐渐变脆。最终，氢的压力和浓度将会导致微裂纹（**图 7**），且会因为氢跟随著裂纹尖端移动而持续增加，直到扣件失效。其结果是，金属将因为大幅降低的负载或应力而破裂或断裂。正是这种较低的断裂强度，使氢脆具有如此的破坏性。不幸的是，对扣件制的造商而言，当钢的强度上升，发生氢脆的可能性也增加。

即使少量的氢也能引起脆化。低至 0.0001%（重量）的氢浓度在某些电镀应用中都会导致脆化。如此少量的氢会因为氢在钢材的应力区域的集中而引起氢脆。

如何侦测出氢脆？

慢弯曲测试和拉力测试可揭露延展性下降而测出氢脆。缺口冲击测试并非每次都能检测出此现象。

最常用於测试螺纹扣件的方法在 ASTM F606、ASTM F519 和 ISO15330 中有说明。这些规范当中，ASTM F606 对扣件制造商而言，是最实际且最经常使用的，因为它可以适用於每批生产的大量样本。对於表面硬化的扣件而言，较适用的程序是第 4.11.5 部份的 ASME B18.6.3。这些属於持续的负载测试，是电镀後测试高强度紧固件的一种品质保证措施。这些测试是施加静态负荷一段固定的时间，从 24 至 200 个小时不等，以测试失效。这些测试的根据将施加的负载缓慢增加直至样本断裂，进而在测试中加入时间的成分。

氢脆消除烘烤的重要考量

浸泡时间：扣件必须处於特定的温度并维持一定的「浸泡」时间，以达到适当的烘烤，但重要的是，浸泡开始之前，需有足够的时间进行升温。这需求对扣件进行加热测试，以确定加热所需的时间。然後加上所需的烘烤时间，以确定总加热时间。

温度均匀性：若要有适当的烘烤，零件的温度必须在整个烘烤期间保持大约 ±8ºC（±15ºF）至 ±10℃（±20ºF）的指定烘烤温度。因此，

maintain this temperature tolerance throughout the entire heating chamber. This should be verified prior to production by performing a temperature uniformity survey in an empty oven. Thermocouples are passed through the heated oven and the temperature is recorded. If any cold spots are identified, they are corrected via adjustment and balancing of the oven. It is prudent and common to require a tolerance of ±8ºC in the empty-oven test in order to provide a safety factor to insure that the required part temperature tolerance (± 8ºC to ± 10ºC) is maintained during actual production. After the empty-oven testing is successfully complete, additional testing is performed to verify the fasteners will reach and maintain the required temperature for the required bake time. This is done by burying thermocouples in the fasteners while simulating the load rate to be experienced during production. The time is recorded during both the heating and the baking.

Pyrometry and Documentation: It is important for quality control purposes that the temperature of the baking oven be recorded continually during production. This allows for more effective failure diagnosis in the event improper baking is suspected as a cause. Many end users (in the automotive industry for example) require this as a quality measure. It is recommended to incorporate a pyrometry standard, such as AMS2750 (latest revision), which dictates the calibration tolerance of instruments, the frequency of oven uniformity surveys, and other important factors. Certain end users will require such a standard be followed.

Oven Selection and Design: In order to achieve a proper and consistent bake, the bake oven must be properly designed for hydrogen embrittlement relief. It is important, for example, that a sufficient volume of recirculated air be utilized to heat the parts up, then maintain the specified bake temperature for the required soak time. In a conveyor style bake oven, a recirculation rate of 8.5 – 11.5 m^3/min (300 - 400 ft^3/minute) for each square foot of conveyor belt yields good result. In a batch style bake oven, 20 to 25 air changes per minute (for example, the recirculation rate in m^3/minute, divided by the oven work chamber volume, in cubic meters) is generally sufficient.

In a conveyorized fastener bake oven the parts are typically loaded several centimeters deep, which makes it difficult for the heated enter to

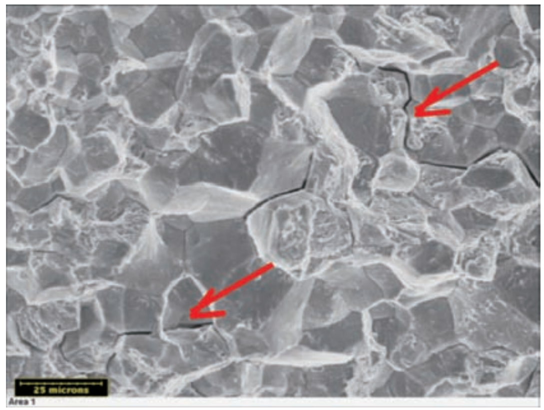

Fig. 7 Microcracks caused by Hydrogen Embrittlement (Courtesy of Sidheshwar Kumar)

图 7 因氢脆所造成的微裂痕

permeate. As a result, the air must be delivered to the parts from both above and below in order to provide uniform heating. This requires air supply ductwork be located both above and below the fasteners carried on the conveyor. Also, it is good practice to utilize multiple heating zones, where each zone has a separate heat source and recirculation system. The first zone (incorporating perhaps ¼ of the oven length, for example) is dedicated to heating up the cold parts to the required soak temperature. The remaining zones provide the necessary soak time. This multiple zone design allows the bake oven to provide consistent results even when the fastener loading (i.e., pounds per hour) varies or different fasteners are baked. ◘

References

1. *ASTM F1940 (Standard Test Method for Process Control Verification to Prevent Hydrogen Embrittlement in Plated or Coated Fasteners), www.astm.org*
2. *TransportersRus (www.t4srus.co.uk)*
3. *Brahimi, Salim "Hydrogen Embrittlement in Steel Fasteners", July, 2014*

烤炉具有在整个加热室维持此温范围的能力，是很重要的。这一点应该在生产前在空炉中进行温度均匀性调查验证之。

热电偶穿过加热的烘箱，且温度被记录下来。如果发现任何冷点，则透过烤炉的调整和平衡加以校正。为谨慎起见，常见的做法是对空炉进行公差 ±8ºC 的试验，以提供一个安全系数，确保所需的零件温度公差（±8℃至±10℃）在实际的生产过程中得以维持。空烘箱测试在成功完成之後，执行进一步的测试以确认扣件将在所规定的烘烤时间内达到并保持所需的温度。这是藉由将热电偶埋入扣件，并在同时模拟生产过程中所经历的负载率来进行。加热和烘烤的过程中都将此时间记录下来。

高温测定及文件纪录：基於品管的目的，烤炉的温度在生产期间持续加以记录是很重要的。如此能在疑有不当烘焙的情况下进行更有效的失效诊断。许多终端用户（例如在汽车行业）需要这种方法做为品管措施。建议纳入一种测温标准，如 AMS2750（最新修订版），决定仪器的校准公差、烤炉温度均匀性测量的频率，以及其他重要因素。某些终端用户将会要求遵循此标准。

烤炉的选择和设计：为了实现适当且一致的烘烤效果，烤炉必须针对氢脆消除适当设计。例如，利用足够体积的再循环空气将零件加热，然後将特定烘烤温度维持在所需的浸泡时间，是很重要的。在传送带式的烤炉中，每平方公尺输送带上 8.5~11.5 立方米 / 分钟（300~400 立方英尺 / 分钟）的再循环率可产生好的结果。在分批式的烤炉中，每分钟有 20 至 25 项空气的变化（例如，立方公尺 / 分钟的再循环率除以立方公尺计算的烤炉作业容积）通常就够了。

在输送带式的扣件烤炉中，零件的装载深度通常为数公分，这使得进入的热能难以渗透。其结果是，空气必须输送到零件的上方和下方，以提供均匀的加热。如此需要空气供应管道位於输送带上承载的扣件上方和下方。此外，使用多个加热区，其中每个区具有独立的热源和再循环系统，是好的做法。第一区（约占烤炉长度的四分之一）专用於将冷却的零件加热到所需的浸泡温度。其馀区域提供必要的浸泡时间。这种多区域的设计使烤炉即使是扣件负荷（即每小时磅数）发生变化，或者烘烤不同的扣件时，也能提供一致的结果。 ◘