什么是“金属氢脆”现象？该如何解决？ What is the "metal hydrogen embrittlement" phenomenon? How should it be solved?

化工活动家 Chemical activist

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导 读 Introduction

在任何电镀溶液中，由于水分子的离解，总或多或少地存在一定数量的氢离子。因此，电镀过程中，**在阴极析出金属（主反应）**的同时，**伴有氢气的析出（副反应）**。析氢的影响是多方面的，其中最主要的是氢脆。氢脆是表面处理中最严重的质量隐患之一，析氢严重的零件在使用过程中就可能断裂，造成严重的事故。表面处理技术人员必须掌握避免和消除氢脆的技术，以使氢脆的影响降低到最低限度。

In any electroplating solution, due to the dissociation of water molecules, a certain amount of hydrogen ions always exist in varying degrees. Therefore, during the electroplating process, while metal is deposited at the cathode (the main reaction), hydrogen gas is also released (a secondary reaction). The effects of hydrogen evolution are multifaceted, with the most significant being hydrogen embrittlement. Hydrogen embrittlement is one of the most serious quality hazards in surface treatment. Parts with severe hydrogen evolution may fracture during use, causing serious accidents. Surface treatment technicians must master the techniques to avoid and eliminate hydrogen embrittlement to minimize its impact to the lowest limit.

什么是“氢脆” What is "Hydrogen Embrittlement"

01

氢脆现象 Hydrogen Embrittlement Phenomenon

氢脆通常表现为 **应力作用下的延迟断裂现象** 。曾经出现过汽车弹簧、垫圈、螺钉、片簧等镀锌件，在装配之后数小时内陆续发生断裂，断裂比例达40%～50%。某特种产品镀镉件在使用过程中曾出现过批量裂纹断裂，曾组织过全国性攻关，制订严格的去氢工艺。另外，有一些氢脆并不表现为延迟断裂现象，例如：电镀挂具（钢丝、铜丝）由于经多次电镀和酸洗退镀，渗氢较严重，在使用中经常出现一折便发生脆断的现象；精锻用的芯棒，经多次镀铬之后，堕地断裂；有的淬火零件（内应力大）在酸洗时便产生裂纹。这些零件渗氢严重，无需外加应力就产生裂纹，再也无法用去氢来恢复原有的韧性。

Hydrogen embrittlement usually manifests as delayed fracture under stress. There have been cases where galvanized parts such as car springs, washers, bolts, and leaf springs have fractured sequentially within a few hours after assembly, with a fracture rate of 40% to 50%. A special product with cadmium-plated parts has experienced batch cracking and fracturing during use, and a national-level research project was organized, and strict dehydrogenation processes were established. In addition, some hydrogen embrittlement does not manifest as delayed fracture, for example: electroplated fixtures (steel wire, copper wire) due to multiple electroplating and acid pickling stripping, have serious hydrogen penetration, and often fracture when bent; core bars used for precision forging, after multiple chrome plating, break when dropped; some heat-treated parts (with large internal stress) produce cracks during pickling. These parts have serious hydrogen penetration, and cracks occur without external stress, and they can no longer be restored to their original toughness by dehydrogenation.

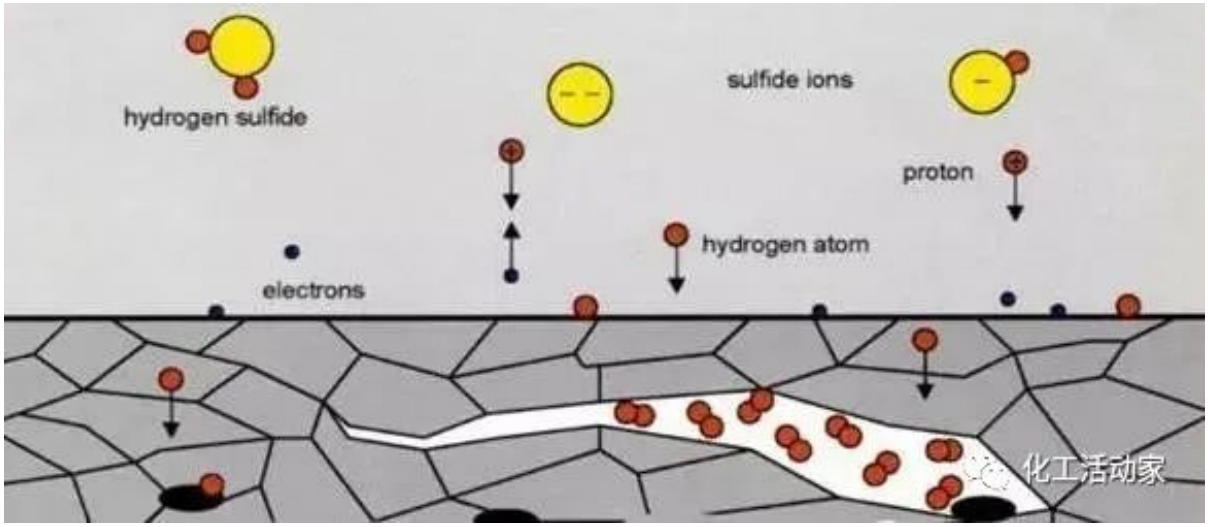
02

氢脆机理 Mechanism of hydrogen embrittlement

延迟断裂现象的产生是由于零件内部的氢向应力集中的部位扩散聚集，应力集中部位的金属缺陷多（原子点阵错位、空穴等）。氢扩散到这些缺陷处，氢原子变成氢分子，产生巨大的压力，这个压力与材料内部的残留应力及材料受的外加应力，组成一个合力，当这合力超过材料的屈服强度，就会导致断裂发生。氢脆既然与氢原子的扩散有

关，扩散是需要时间的，扩散的速度与浓差梯度、温度和材料种类有关。因此，氢脆通常表现为延迟断裂。

The occurrence of delayed fracture is due to the diffusion and accumulation of hydrogen inside the part to the stress concentration areas, where there are many metal defects (such as atomic lattice displacement, vacancies, etc.). When hydrogen diffuses to these defects, hydrogen atoms become hydrogen molecules, generating enormous pressure. This pressure, combined with the residual stress within the material and the external stress applied to the material, forms a resultant force. When this resultant force exceeds the yield strength of the material, fracture occurs. Since hydrogen embrittlement is related to the diffusion of hydrogen atoms, diffusion requires time, and the diffusion rate is related to the concentration gradient, temperature, and material type. Therefore, hydrogen embrittlement usually manifests as delayed fracture.



氢原子具有最小的原子半径，容易在钢、铜等金属中扩散，而在镉、锡、锌及其合金中氢的扩散比较困难。镀镉层是最难扩散的，镀镉时产生的氢，最初停留在镀层中和镀层下的金属表层，很难向外扩散，去氢特别困难。经过一段时间后，氢扩散到金属内部，特别是进入金属内部缺陷处的氢，就很难扩散出来。常温下氢的扩散速度相当缓慢，所以需要即时加热去氢。温度升高，增加氢在钢中的溶解度，过高的温度会降低材料的硬度，所以镀前去应力和镀后去氢的温度选择，必须考虑不致于降低材料硬度，不得处于某些钢材的脆性回火温度，不破坏镀层本身的性能。

Hydrogen atoms have the smallest atomic radius and are easy to diffuse in metals such as steel and copper, while hydrogen diffusion is relatively difficult in cadmium, tin, zinc, and their alloys. Cadmium plating is the most difficult to diffuse. The hydrogen produced during cadmium plating initially remains in the plating layer and the metal surface below it, and it is difficult to diffuse outward, making dehydrogenation particularly difficult. After a period of time, hydrogen diffuses into the interior of the metal, especially into the internal defects of the metal, which is difficult to diffuse out. At room temperature, the diffusion rate of hydrogen is quite slow, so immediate heating for dehydrogenation is required. As the temperature rises, it increases the solubility of hydrogen in steel, and excessive temperature will reduce the hardness of the material. Therefore, the temperature selection for stress relief before plating and dehydrogenation after plating must be considered to avoid reducing the hardness of the material, not being at the brittleness tempering temperature of certain steel grades, and not damaging the performance of the plating layer itself.

避免和消除“氢脆”措施 Measures to avoid and eliminate "hydrogen embrittlement"

01

减少金属中渗氢量 Reducing the amount of hydrogen penetration in metals

在除锈和氧化皮时，尽量采用吹砂除锈，若采用酸洗，需在酸洗液中添加若丁等缓蚀剂；在除油时，采用化学除油、清洗剂或溶剂除油，渗氢量较少，若采用电化学除油，先阴极后阳极；在电镀时，碱性镀液或高电流效率的镀液渗氢量较少。

When descaling and removing oxide scale, it is recommended to use blast cleaning as much as possible; if acid pickling is used, it is necessary to add inhibitors such as rutile to the acid pickling solution; when degreasing, use chemical degreasing, detergents, or solvent degreasing, which has less hydrogen penetration. If electrochemical degreasing is used, it should be done first cathodically and then anodically; during electroplating, alkaline plating solutions or plating solutions with high current efficiency have less hydrogen penetration.

02

采用低氢扩散性和溶解度的镀涂层 Using coatings with low hydrogen diffusion and solubility

一般认为，在电镀Cr、Zn、Cd、Ni、Sn、Pb时，渗入钢件的氢容易残留下来，而Cu、Mo、Al、Ag、Au、W等金属镀层具有低氢扩散性和低氢溶解度，渗氢较少。在满足产品技术条件要求的情况下，可采用不会造成渗氢的涂层，如达克罗涂覆层可以代替镀锌，不会发生氢脆，耐蚀性提高7～10倍，附着力好，膜厚6～8um,相当于较薄的镀锌层，不影响装配。

It is generally believed that hydrogen 渗入 steel parts during electroplating of Cr, Zn, Cd, Ni, Sn, Pb is easy to remain, while metal coatings such as Cu, Mo, Al, Ag, Au, W have low hydrogen diffusion and low hydrogen solubility, with less hydrogen penetration. Under the condition of meeting the technical requirements of the product, coatings that do not cause hydrogen penetration can be used, such as the Dacromet coating can replace galvanizing, which does not cause hydrogen embrittlement, improves corrosion resistance by 7 to 10 times, has good adhesion, a film thickness of 6 to 8 μm, which is equivalent to a relatively thin galvanized layer, and does not affect assembly.

03

镀前去应力和镀后去氢 Stress relief before plating and hydrogen removal after plating

若零件经淬火、焊接等工序后内部残留应力较大，镀前应进行回火处理，减少发生严重渗氢的隐患。

If the internal residual stress of the part is relatively large after processes such as quenching and welding, tempering treatment should be carried out before plating to reduce the hidden danger of serious hydrogen penetration.

对电镀过程中渗氢较多的零件原则上应尽快去氢，因为镀层中的氢和表层基体金属中的氢在向钢基体内部扩散，其数量随时间的延长而增加。新的国际标准草案规定“最好在镀后1h内，但不迟于3h,进行去氢处理”。国内也有相应的标准，对电镀锌前、后的去氢处理作了规定。电镀后去氢处理工艺广泛采用加热烘烤，常用的烘烤温度为150～300℃，保温2～24h。具体的处理温度和时间应根据零件大小、强度、镀层性质和电镀时间的长短而定。去氢处理常在烘箱内进行。镀锌零件的去氢处理温度为110～220℃，温度控制的高低应根据基体材料而定。对于弹性材料、0.5mm以下的薄壁件及机械强度要求较高的钢铁零件，镀锌后必须进行去氢处理。为了防止“镉脆”，镀镉零

件的去氢处理温度不能太高，通常为180～200℃。

Parts with excessive hydrogen penetration during electroplating should be dehydrogenated as soon as possible in principle, as hydrogen in the coating and in the surface matrix metal of the base metal diffuses into the steel matrix, and its quantity increases with time. The new draft international standard stipulates that "dehydrogenation treatment should be carried out within 1 hour after plating, but not later than 3 hours." There are also corresponding domestic standards that specify dehydrogenation treatment before and after electroplating zinc. The dehydrogenation treatment process after electroplating commonly uses heating and baking, with the usual baking temperature ranging from 150 to 300°C, and keeping warm for 2 to 24 hours. The specific treatment temperature and time should be determined according to the size, strength, coating properties, and electroplating duration of the parts. Dehydrogenation treatment is often carried out in an oven. The dehydrogenation treatment temperature for zinc-plated parts is 110 to 220°C, and the temperature control should be based on the base material. For elastic materials, thin-walled parts with a thickness of less than 0.5mm, and steel parts with high mechanical strength requirements, dehydrogenation treatment must be carried out after zinc plating. To prevent "cadmium brittleness," the dehydrogenation treatment temperature for cadmium-plated parts should not be too high, usually 180 to 200°C.

注意事项 Precautions

材料强度越大，其氢脆敏感性也越大，这是表面处理技术人员在编制电镀工艺规范时必须明确的基本概念。国际标准要求抗拉强度σｂ>105kg/mm2的钢材，要进行相应的镀前去应力和镀后去氢处理。法国航空工业对屈服强度σｓ>90kg/mm2的钢件就要求作相应去氢处理。

The greater the material strength, the greater the hydrogen embrittlement sensitivity, which is a basic concept that surface treatment technicians must be clear about when compiling electroplating process specifications. The international standard requires that steel with tensile strength σb>105kg/mm2 undergo corresponding pre-plating stress relief and post-plating dehydrogenation treatment. The French aviation industry requires corresponding dehydrogenation treatment for steel parts with yield strength σs>90kg/mm2.

由于钢材强度与硬度有很好的对应关系，因此，用材料硬度来判断材料氢脆敏感比用强度来判断更为直观、方便。因为一份完善的产品图和机加工工艺都应标注钢材硬度。在电镀中我们发现钢的硬度在HRC38左右时开始呈现氢脆断裂的危险。对高于HRC43的零件，镀后应考虑去氢处理。硬度为HRC60左右时，在表面处理之后必须立即进行去氢处理，否则在几小时之内钢件会开裂。

Since there is a good correlation between the strength and hardness of steel, it is more intuitive and convenient to judge the hydrogen embrittlement sensitivity of materials by hardness than by strength. Because a complete product drawing and machining process should indicate the hardness of the steel. In electroplating, we found that the steel starts to show the risk of hydrogen embrittlement fracture when the hardness is about HRC38. For parts with hardness above HRC43, dehydrogenation treatment after plating should be considered. When the hardness is about HRC60, dehydrogenation treatment must be carried out immediately after surface treatment, otherwise the steel parts will crack within a few hours.

除了刚才硬度还应考虑： In addition to the hardness mentioned just now, the following should also be considered:

①零件的使用安全系数：安全重要性大的零件，应加强去氢；

① The safety factor of parts: Parts with high safety importance should be strengthened in dehydrogenation;

②零件的几何形状：带有容易产生应力集中的缺口，小R等的零件应加强去氢；

② The geometric shape of parts: Parts with notches prone to stress concentration, small R, etc., should be strengthened in dehydrogenation;

③零件的截面积：细小的弹簧钢丝、较薄的片簧极易被氢饱和，应加强去氢；

③ The cross-sectional area of parts: Fine spring steel wire, thin leaf springs, etc., are easily saturated with hydrogen and should be strengthened in dehydrogenation;

④零件的渗氢程度：在表面处理中产生氢多、处理时间长的零件，应加强去氢；

④ The degree of hydrogen penetration of parts: Parts that produce more hydrogen and have longer treatment times during surface treatment should be strengthened in dehydrogenation;

⑤镀层种类：如镀镉层会严重阻挡氢向外扩散，所以要加强去氢；

⑤Type of coating: Coating with cadmium will severely block the diffusion of hydrogen outward, so it is necessary to strengthen dehydrogenation;

⑥零件使用中的受力性质：当零件受到高的张应力时应加强去氢，只受压应力时不会产生氢脆；

⑥Nature of stress on parts in use: When parts are subjected to high tensile stress, it is necessary to strengthen dehydrogenation, while under compressive stress, hydrogen embrittlement will not occur;

⑦零件的表面加工状态：对冷弯、拉伸、冷扎弯形、淬火、焊接等内部残留应力大的零件，不仅镀后要加强去氢，而且镀前要去应力；

⑦Surface processing state of parts: For parts with high internal residual stress due to cold bending, stretching, cold rolling bending, quenching, welding, etc., it is not only necessary to strengthen dehydrogenation after plating but also to remove stress before plating;

⑧零件的历史情况：对过去生产中发生过氢脆的零件应特别加以注意，并作好相关记录。

⑧Historical condition of parts: Special attention should be paid to parts that have experienced hydrogen embrittlement in past production, and relevant records should be made.

去氢脆 Eliminate Hydrogen Embrittlement

主要原因是电镀工艺中导致的金属“氢化”现象导致的，而你用的不合格品呢并不是电镀工艺本身有问题，因为电镀（真空镀除外）本来就会造成金属氢化，但是目前有许多金属表面处理商都去掉了最后一个工艺（特别是对于弹性元件很致命的）：那就是“去氢处理”工艺，也就是说正常情况下，对于有强度要求的金属零件需要完成去氢后才能交给用户的，但是为了节省生产成本，而用户又不懂的情况下或者从来没有要求过、验收过的情况下，省略这一工

艺可以节省5~15%的成本呢。所以你感觉到电镀后的螺栓、弹垫等零件在电镀处理后“变脆”了。

The main reason is the "hydrogenation" phenomenon caused by electroplating process, and the unqualified products you use are not due to the problem of electroplating process itself, because electroplating (except vacuum plating) will naturally cause metal hydrogenation. However, at present, many metal surface treatment companies have removed the last process (especially for elastic components, which is very fatal): that is, the "dehydrogenation" process. That is to say, under normal circumstances, for metal parts with strength requirements, it is necessary to complete the dehydrogenation before delivering them to the users. But in order to save production costs, and in the case that the users are not aware of it or have never required or inspected it, omitting this process can save 5~15% of the cost. Therefore, you feel that the bolts, spring washers, and other parts become brittle after electroplating.

一般地说：对于有强度要求的金属零件的去氢处理要求是：120度~220度高温保持1~2小时（电镀结束后），具体情况需要按照零件要求来控制。

Generally speaking, the dehydrogenation treatment requirements for metal parts with strength requirements are: maintain a high temperature of 120 to 220 degrees Celsius for 1 to 2 hours (after electroplating), and the specific conditions need to be controlled according to the requirements of the parts.