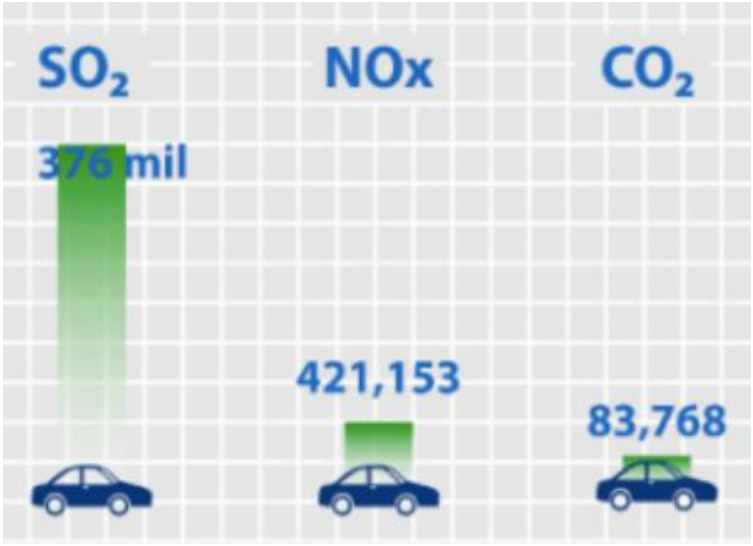
船用烟气净化系统的腐蚀性

Corrosion in marine exhaust gas cleaning systems

大型游轮排放量与汽车排放量对比

Emissions from a large cruse ship compared to the equivalent number of cars

Source Worldmaritimeaffairs/Nabu/
Axel Friedrich 2012

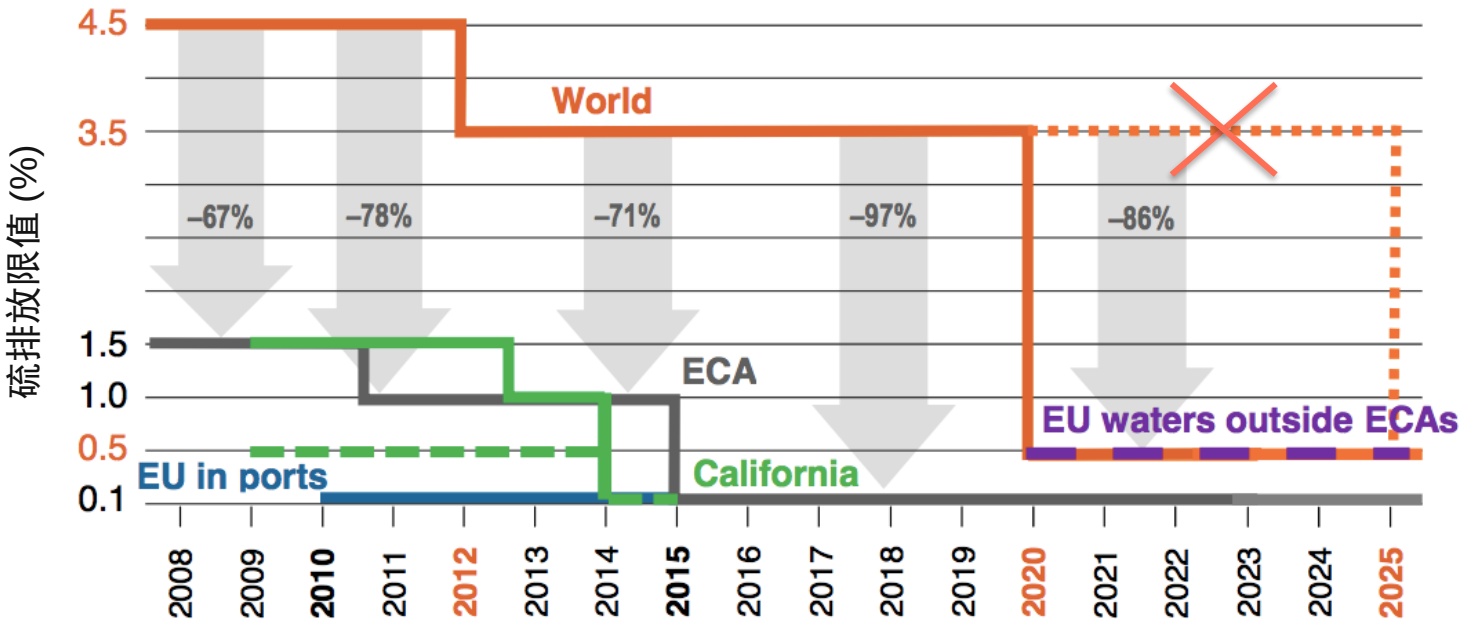


2020年全球硫排放上限

The 2020 Global Sulphur Cap

联合国国际海事组织(IMO)和海洋环境保护委员会(MEPC)负责处理与海洋污染有关的问题。

International Maritime Organization (IMO) and Marine Environment Protection Committee (MEPC) belong to the United Nations, they deal with marine pollution related.



国际防止船舶造成污染公约（MARPOL）附则VI限制船舶废气排放，包括氮氧化物（NOx）、硫氧化物（SOx），

MARPOL (The International Convention for the Prevention of Pollution from Ships) Annex VI limits ship exhaust gas emissions including nitrogen oxides (NOx), sulfur oxides (SOx),

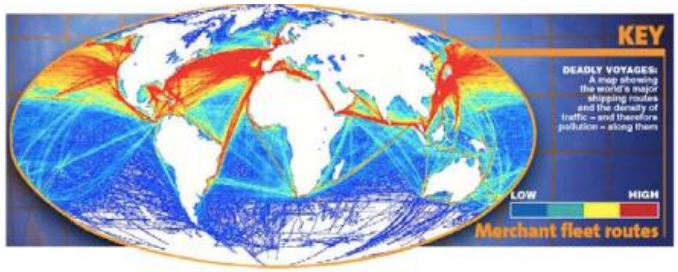
MARPOL公约附则6规定了排放控制区，以进一步减少指定海域的排放。

MARPOL Annex VI introduced ECAs (Emission Control Areas) to reduce emissions further in designated sea areas.

中国排放控制区

控制硫排放行动计划

Strategies to Control Sulfur Emissions



MARPOL Annex VI

规避排放控制区

决策

采用低硫燃料

采用LNG双燃料发动机

安装洗涤器

Bunker Prices ($/metric tons)	HFO	MGO
Global Average	317.50	527.50
Americas Average	341.00	594.00
APAC Average	348.50	616.50
EMEA Average	347.00	537.00

*Information adopted from Ship&Bunker on August 16th, 2017
**Demand driving fuel price

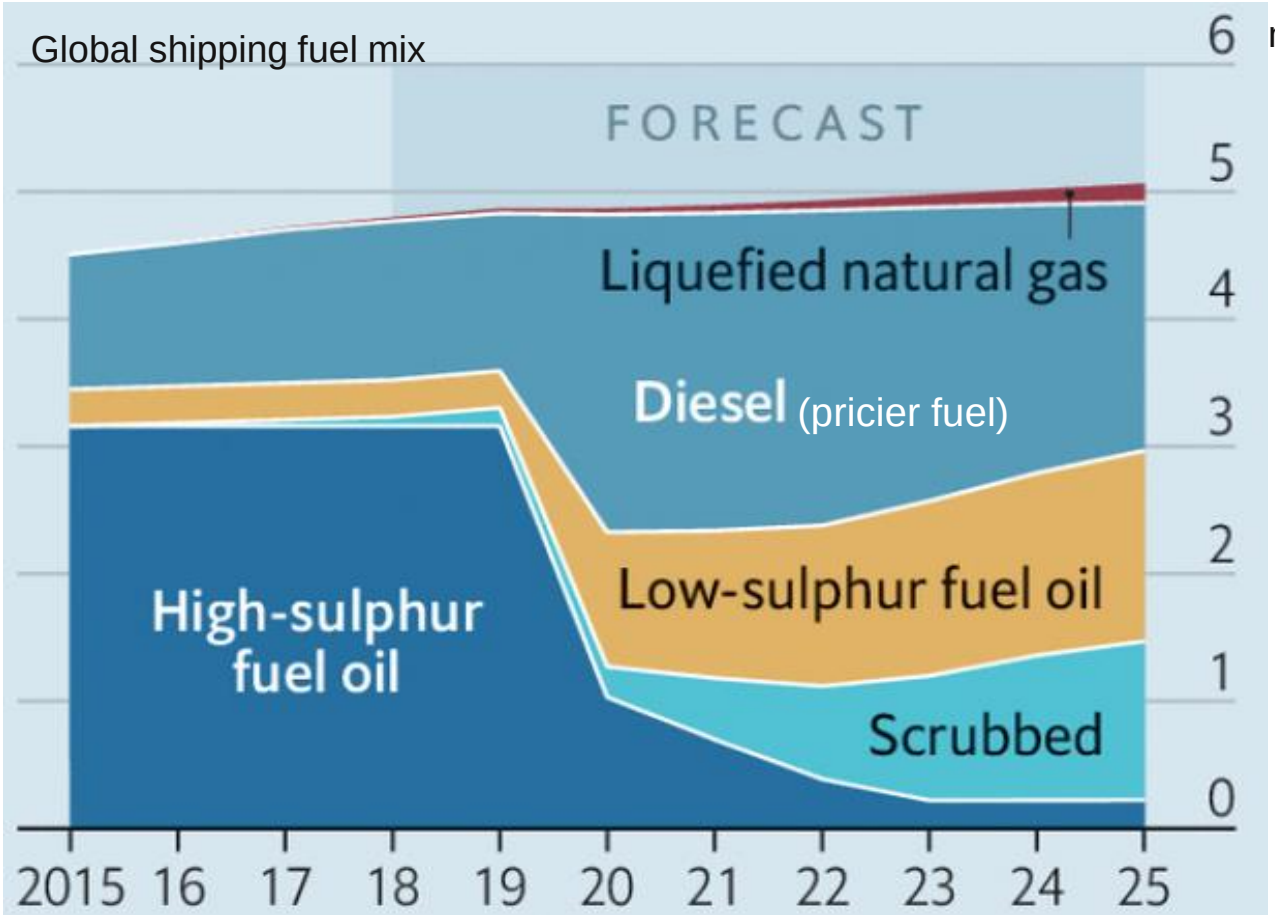
Source University of California - Riverside

控制硫排放行动计划

Strategies to Control Sulfur Emissions

全球9万艘商船中，大约只有2000艘可以在最后期限前达到规定要求

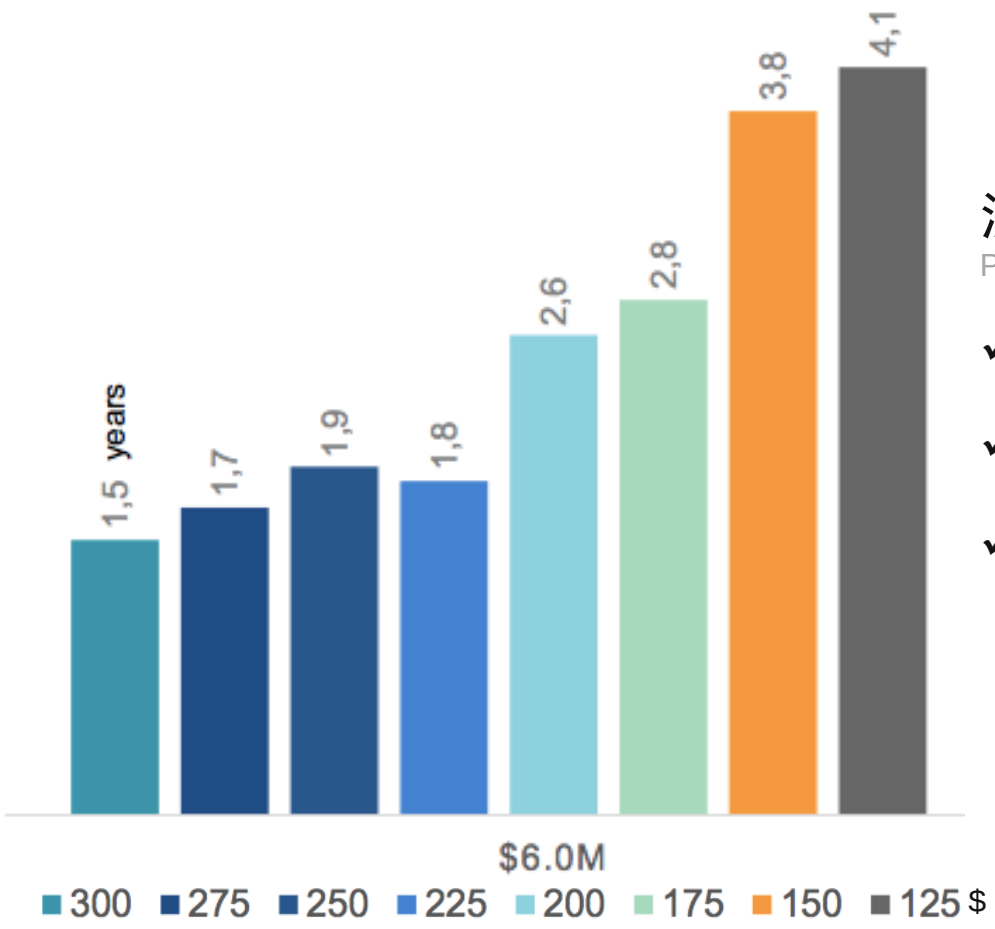
Only around 2,000 of 90,000 commercial vessels on the world's seas will have them by the deadline



Source The Economist/Goldman Sachs 2018

按可变燃料差价实现600万美元投资盈亏平衡的时间

YEARS TO BREAK-EVEN $6.0M INVESTMENT BY VARIABLE FUEL SPREAD



Source Jon Helge Ulstein- Wilhelmsen Ship Management

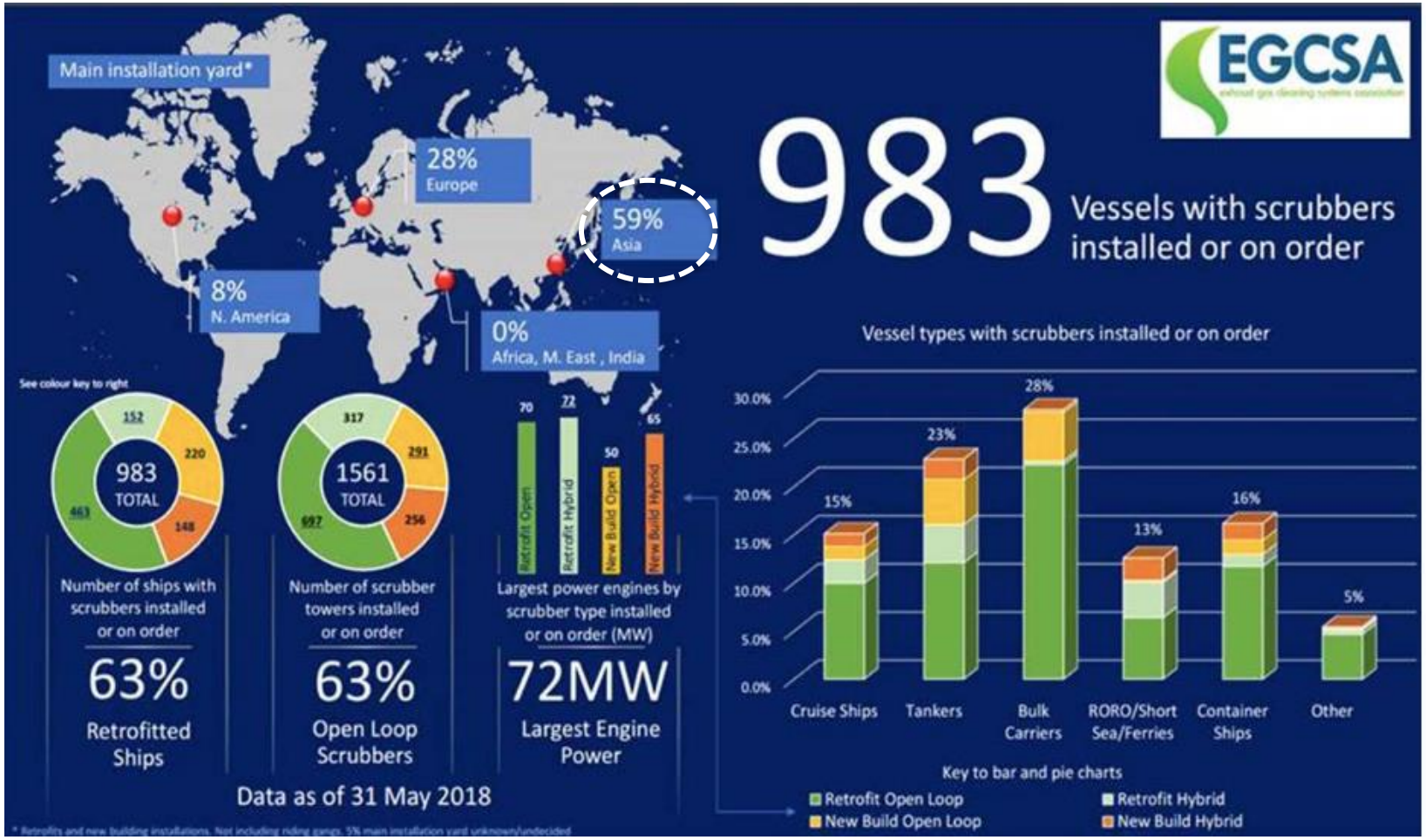
洗涤器的投资回收时间取决于

Payback time for a scrubber depends upon

- ✓ 设备制造和安装成本
  capital and installation cost of the system,
- ✓ 排放控制区年度燃料消耗
  annual fuel consumption in ECAs and
- ✓ 船用馏分燃料和普通燃料之间的价差
  the price differential between distillate fuel and the normal fuel used on the vessel.

废气净化协会（EGCSA）分析结果

Exhaust Gas Cleaning Association analysis

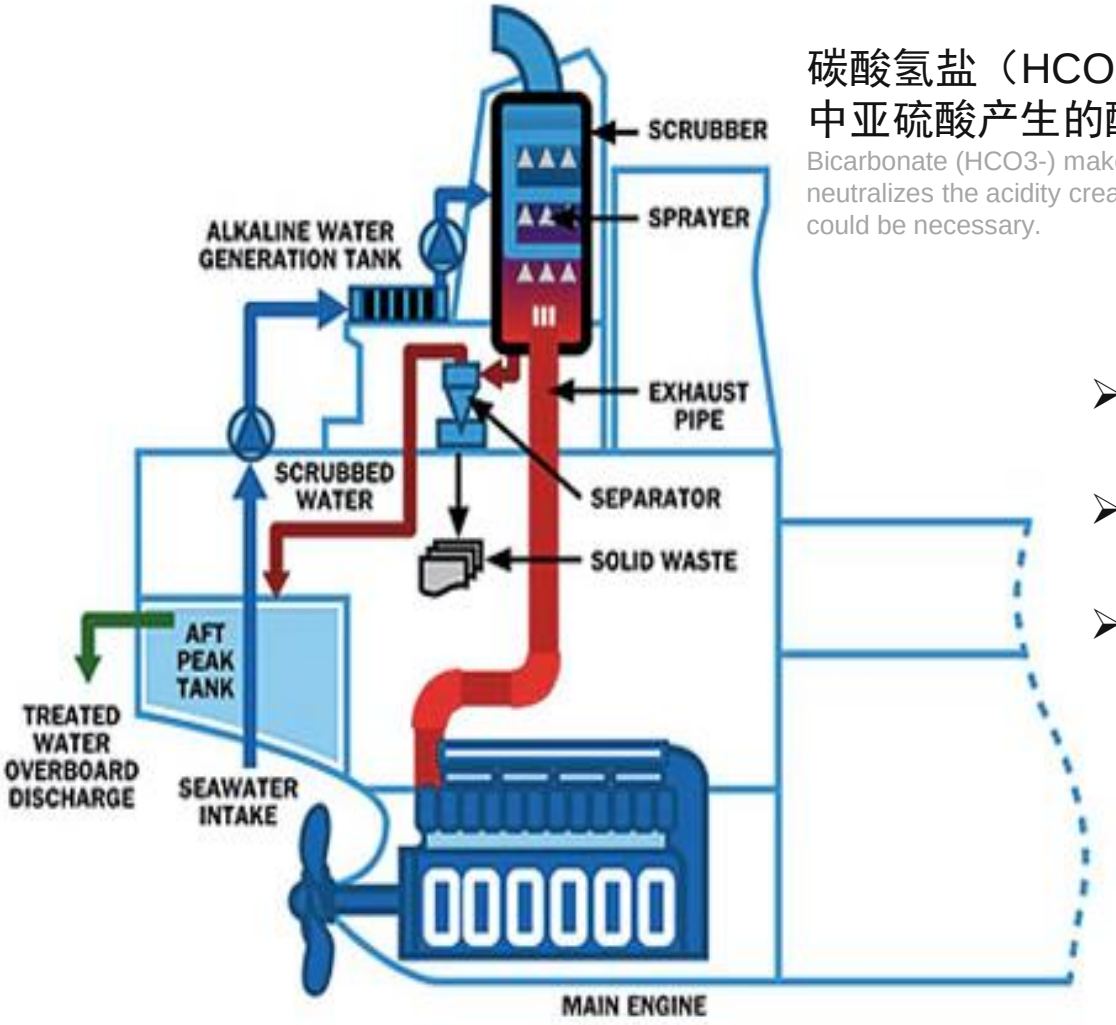


湿法洗涤器：去除船舶主机废气中的Sox

Wet scrubbers: SOx Removal Technologies from Marine Exhaust Gases Generated by Main Engines

海水以微小液滴的形式喷射到洗涤塔中，二氧化硫溶解成亚硫酸（H_2SO_3）

The sea water is sprayed into the scrubber tower in tiny droplets, The dissolved sulfur dioxide turns into sulfurous acid (H2SO3)



碳酸氢盐（HCO3-）使海水略呈碱性，中和洗涤器中亚硫酸产生的酸性。有时也会用到NaOH或MgO。

Bicarbonate (HCO3-) makes seawater slightly alkaline, used in a scrubber it neutralizes the acidity created by the sulfurous acid. Few helpers, NaOH or MgO, could be necessary.

- 开环洗涤器（洗涤介质：海水

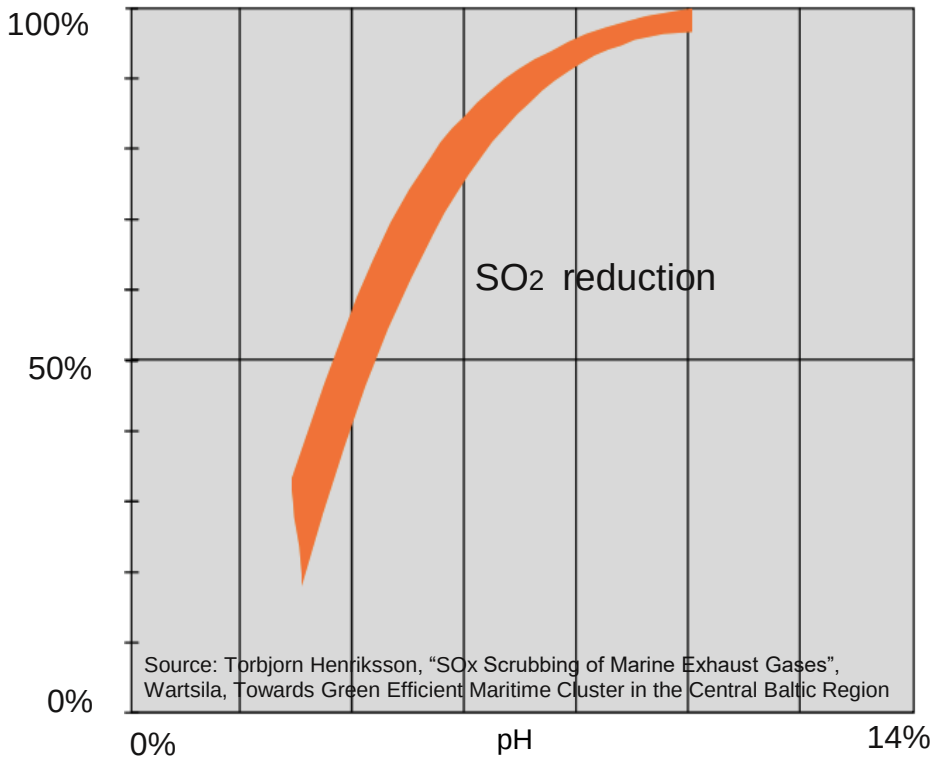
  Open-Loop Scrubbers (Scrubbing Medium: Seawater
- 闭环洗涤器（洗涤介质：NaOH

  Closed-Loop Scrubbers (Typical Scrubbing Medium: Caustic Soda (NaOH)
- 两用洗涤器（运行模式：开-闭或闭-开）

  Hybrid Scrubbers (Operation as Either O-L or C-L)

中和二氧化硫

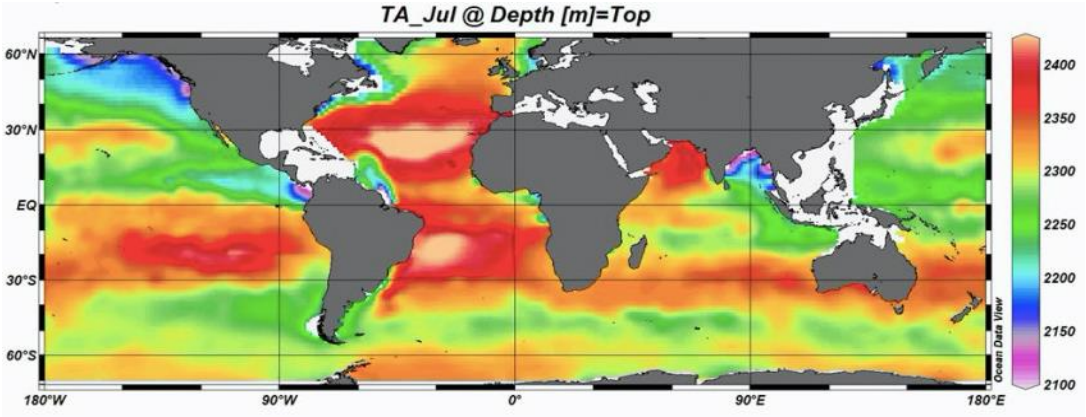
SO2 Neutralization



适当的pH值

Occurs with Proper pH either by:

- ✓加碱
  Dosing of Alkali
- ✓使用足量的海水
  Using Sufficient SW Mass



Open sea (0-15m) alkalinity Surface data

船用洗涤器-恶劣环境 Marine scrubbers – a hostile environment

船舶管理巨头--中英船舶管理集团（Anglo Eastern）首席执行官Bjørn Højgaard“洗涤器是敏感设备，处在船舶烟囱恶劣的高温、酸性环境中”

Bjørn Højgaard, CEO of ship-management giant Anglo-Eastern “scrubbers are sensitive pieces of equipment sitting in the hostile, hot and acidy environment of a ship’s funnel”

- ✓ 海水变热，高达80ºC，Cl-含量约20000 ppm。在pH值为7.5-8.4，并有缓冲电位的情况下，当有足够的酸时，pH值会呈酸性，降至2-4。
  Seawater becomes hot, up to 80ºC, and contains ~20,000 ppm Cl^-. While pH is naturally ~7.5-8.4 and has a buffering potential, it can become acidic with sufficient acid input, down to perhaps 2-4.
- ✓ 进气温度250-450ºC。如果没有旁路管道且没有通水，双相不锈钢可能脆化。谨用塑料和人造橡胶。
  Inlet gas temperature can be 250-450ºC. If no bypass duct, duplex SS can embrittle if the water is not turned on. Plastics and elastomers have to be used with caution.
- ✓ 在低pH值、高污染的高温环境下发生冷凝
  The condensate can form at high temperatures with low pH and large contamination levels
- ✓ 由于封闭区域的蒸发效应（缝隙腐蚀），Cl-含量可达到100.000 ppm
  Due to evaporation in case of occluded areas (crevice corrosion) Cl^- content can reach 100.000 ppm
- ✓ 船长/轮机员不习惯操作控制系统相当严密的化工设备
  Ship captains / marine engineers are not used to operating what is in effect a chemical process with fairly tight controls.

船用洗涤器 – 选材

Marine scrubbers – material selection

1) 洗涤器腐蚀类型 Types of corrosion in scrubbers:

   - 点蚀和缝隙腐蚀
     pitting and crevice corrosion

     注：洗涤器不存在均匀腐蚀
     Note: not general corrosion

2) 影响洗涤器耐蚀性的重要因素 Primary factors affecting corrosion resistance in scrubbers are:

   - 温度 temperature
   - pH值（酸度） pH (acidity)
   - 氯化物(和氟化物*)含量（海水 ~19,000ppm Cl-)
     chloride (and fluoride*) content (seawater ~19,000ppm Cl-)
   - 氧化杂质（氧、铁和锰离子等）
     oxidizing impurities (oxygen, ferric and manganic ions, etc.)

   * 氟化物对船用洗涤器是否有影响目前还不清楚
     Fluoride not known to be a factor in marine scrubbers

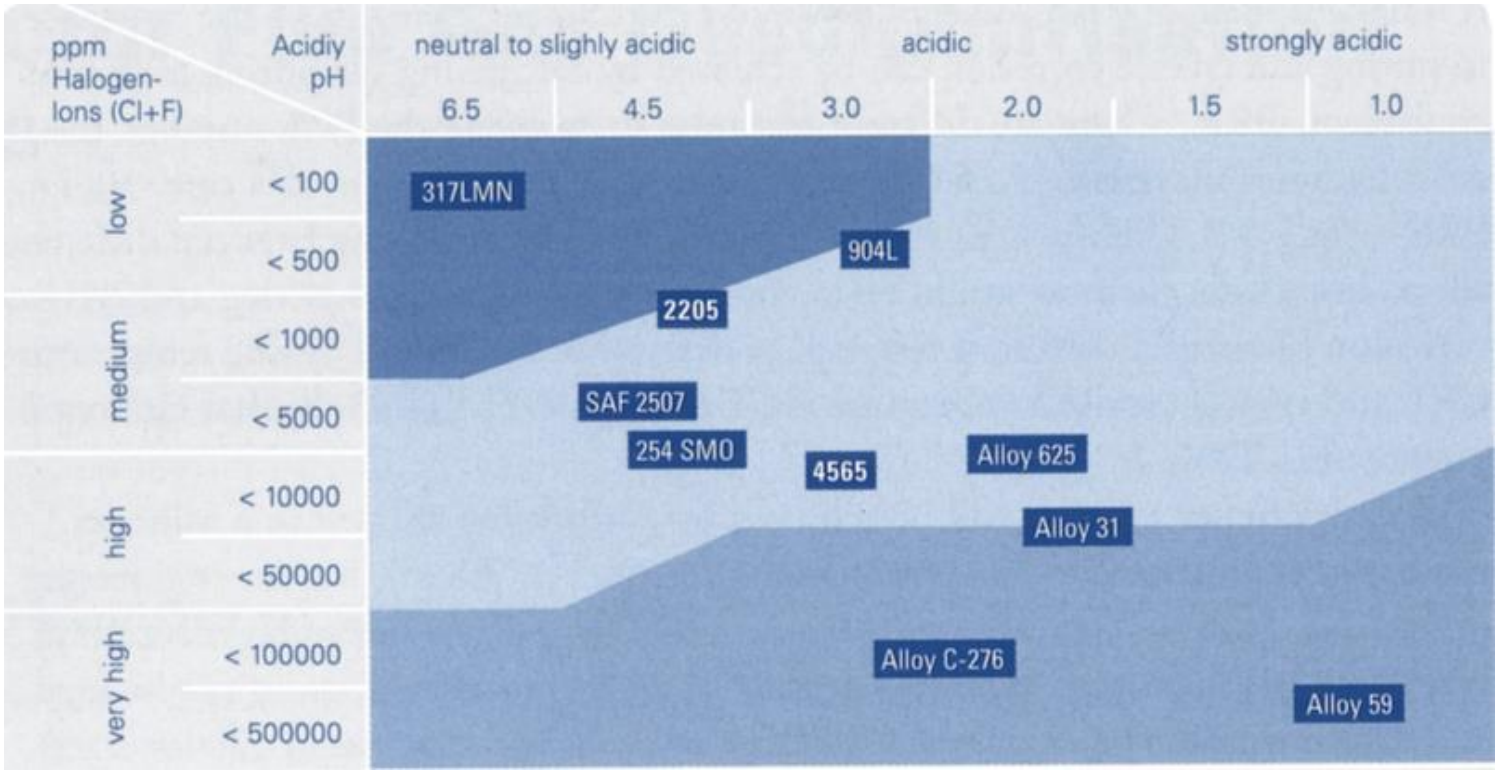
船用洗涤器 – 选材

Marine scrubbers – material selection

General chart

Which alloys are generally suitable where. This is for coal-fired power plant scrubbers.

pH vs. halogen Content



Source Outokumpu – temperature range 50-70 C

用海水洗涤的船用洗涤器需要高合金材料

Marine Scrubbers using seawater for scrubbing liquor should need high alloyed materials.

船用洗涤器 –选材 Marine scrubbers – material selection

目前使用的材料 Materials known to be used

- ✓ 22 Cr Duplex
- ✓ 25 Cr Duplex
- ✓ 6%Mo - e.g. 254 SMO
- ✓ 7%Mo
- ✓ Alloy 31
- ✓ Alloy 59
- ✓ Other C-alloys - e.g. C-276

欧洲有些洗涤器制造厂家使用6%Mo、7%Mo、合金31和C型合金（C-276、C-22、C-59等）。有一些可能使用双相不锈钢，主要是超级双相合金

In Europe, there are several scrubber manufacturers who use alloys such as 6%Mo, 7%Mo, Alloy 31, C-type alloys (C-276, C-22, C-59 etc.). There may be some use of duplex ss, mostly superduplex alloys.

中国制造厂家最常用的材料是2205. In China, the most common alloy used is 2205.

A. 局部腐蚀比一般腐蚀更不可预测，且更具破坏性
   Localized corrosion is less predictable than general corrosion and is more damaging

B. 目前还没有船用洗涤器系统腐蚀数据的公开文献
   Open Literature Has Not yet Information On Corrosion Data Of Marine Scrubber System.

NACE (National Association of Corrosion Engineers) – March 2019 Task Group, TG575
https://www.surveymonkey.com/r/RZFTYG7

船用洗涤器 – 腐蚀问题

Marine scrubbers – what corrosion issues?

2019年11月：洗涤器使用十年。Ficaria Seaways号装有阿尔法拉瓦尔系统，在北海硫氧化物排放控制区（SECA）航行了10年（5万个小时）

November 2019: A decade of scrubber use. Ficaria Seaways fitted with an Alfa Laval system, operates inside the North Sea SECA sine 10 years (50,000 running hours)

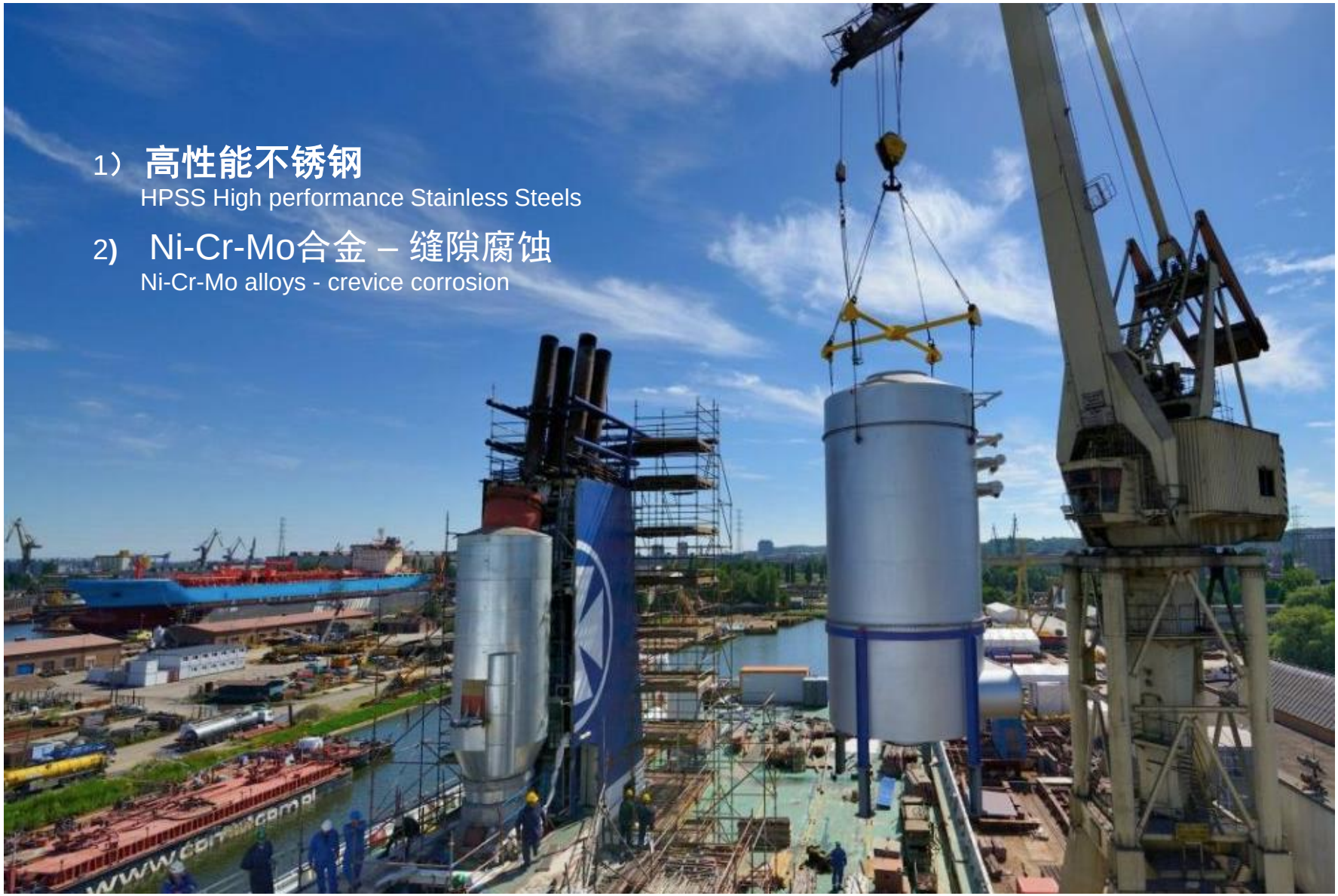
船用洗涤器 – 腐蚀问题

Marine scrubbers – what corrosion issues?

2019年10月：亚洲航运杂志《Splash》仅上个月就发生6起洗涤器故障。

October 2019: Splash, the Asia Shipping magazine, has counted six scrubber failures in the last month alone.

制作注意事项 Precautions for the fabrication



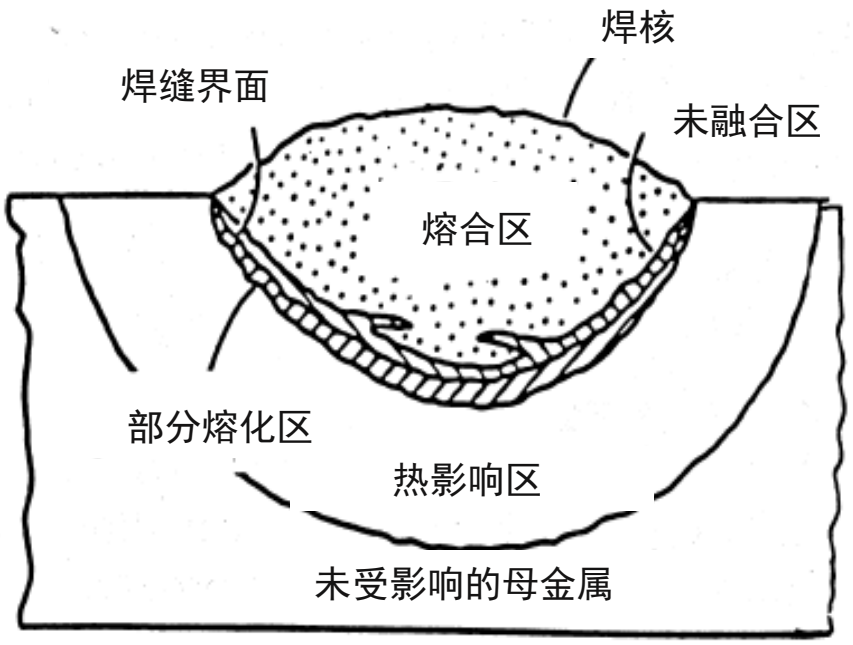
不锈钢实心板
Stainless Steel Solid Plates

奥氏体不锈钢 – 高性能奥氏体不锈钢未混合区
Austenitic stainless steels - Unmixed Zone in HPASS

不锈钢焊缝组织比热影响区包围的凝固熔合区更复杂
The microstructure of a stainless steel weld is more complicated than a solidified fusion zone bounded by a heat-affected zone.

奥氏体不锈钢焊缝金相组织由以下四个区组成：
Austenitic stainless steel welds have a microstructure that consists of four regions:

- fusion zone 熔合区
- unmixed zone 未熔合区
- partially melted zone 部分熔化区
- heat-affected zone 热影响区



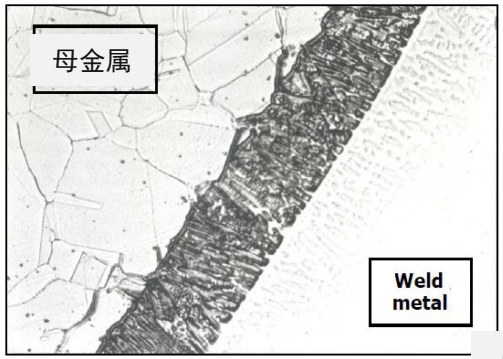
Source: Savage, W. F., Nippwa, E. F. and Szekeres, E. S. "A Study of Weld Interface Phenomena In a Low Alloy Steel," Welding Journal, 55(9), Sept. 1976

高性能奥氏体不锈钢未混合区

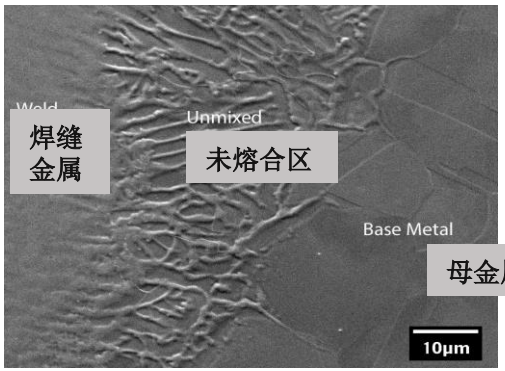
Unmixed Zone in HPASS

Unmixed zone in 6% Mo super austenitic stainless steels

6%Mo超级奥氏体不锈钢未混合区



焊缝金属



Source: Metrode Products Ltd., “Filler Materials for 6% Mo Superaustenitic Stainless Steels,“ August, 2005.

Unmixed zone in a 6% Mo HPASS (N08367)

6%Mo高性能奥氏体不锈钢(N08367)

Source: TMR Stainless

奥氏体不锈钢未混合区的重要特性

- 未混合区具有母材的成分，其显微结构由一个与自熔焊接非常相似的凝固树枝状结构组成。
  The unmixed zone has the composition of the base metal and a microstructure that consists of an as-solidified dendritic structure very similar to an autogenous weld.
- 未混合区未出现填充金属稀释
  The unmixed zone has no filler metal dilution.
- 由于合金元素的微观偏析，特别是钼偏析，未混合区的耐蚀性低于母材
  The unmixed zone has reduced corrosion resistance compared to the base metal because of the micro-segregation of alloying elements, particularly Mo segregation.

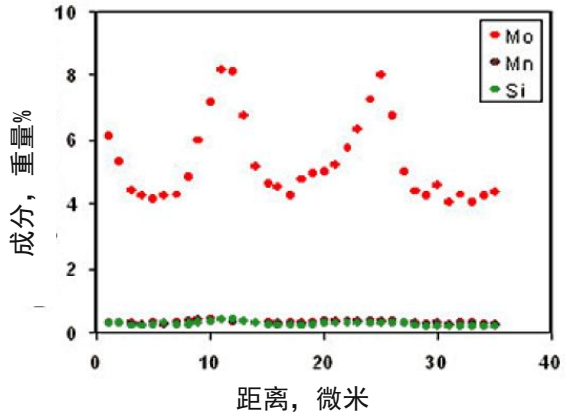
N08367自动TIG焊缝的Mo偏析

As solidified 6% Mo HPASS has a microstructure with dendrite cores depleted in Mo.

凝固态6%Mo HPASS的显微组织呈现贫钼枝晶核

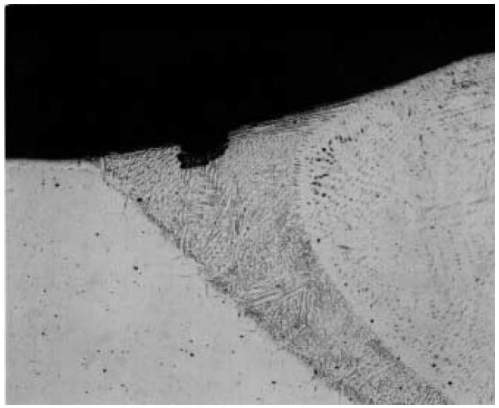
The depleted Mo content is in the range of 4%.

贫钼量在4%左右



Source: J. N. DuPont, “Welding Superaustenitic Stainless Steel for Advanced Double Hull Naval Combatants”, www.lehigh.edu

未混合区选择性侵蚀



Source: P. Stenvall, M. Liljas and B. Wallén, “Performance Of High Molybdenum Superaustenitic Stainless Steel Welds In Harsh Chloride Environments”, NACE Corrosion 96 paper 419

用于6%Mo HPASS的过匹配合金焊料

Over-Alloyed Filler Metals For 6% Mo HPASS

合金	625 (ERNi-CrMo-3)	276 (ERNiCrMo-4)	22 (ERNiCrMo-10)	59 (ERNiCrMo-13)
Cr	22.0	15.0	22.0	23.0
Mo	9.0	16.0	13.0	16.0
Fe	4.0	5.0	4.0	1.0
W	—	4.0	3.0	---
C	0.05	0.01	0.01	0.01
Nb	3.5	---	---	---

高钼焊料可以补偿熔合区的钼偏析，使贫钼区的钼含量保持在6%以上。

A high Mo-bearing filler metal can compensate for the Mo segregation in the fusion zone and keep the Mo content in the depleted regions above 6%

不锈钢实心板 Stainless Steel Solid Plates

双相不锈钢 – 避免金属间相

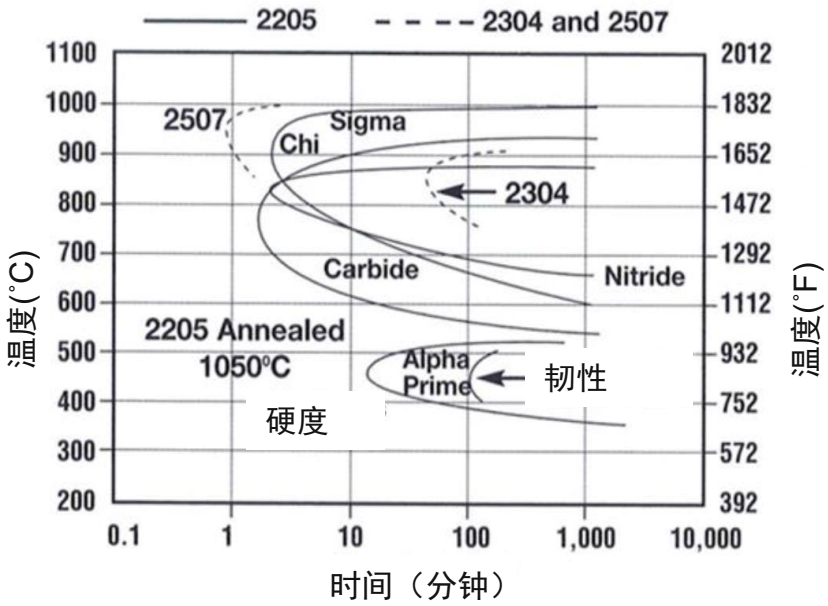
Duplex stainless steels - avoiding intermetallic phases

金属间化合物、氮化物和碳化物 = 耐腐蚀性、延展性和韧性损失

Intermetallics, nitrides carbides = loss of corrosion resistance, ductility, toughness

α’ =延性和韧性损失

Alpha prime = loss of ductility & toughness

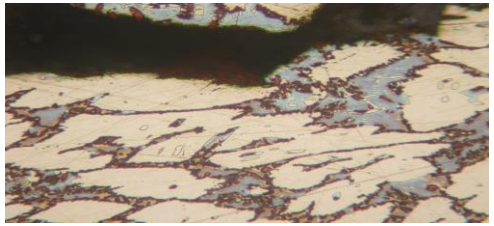


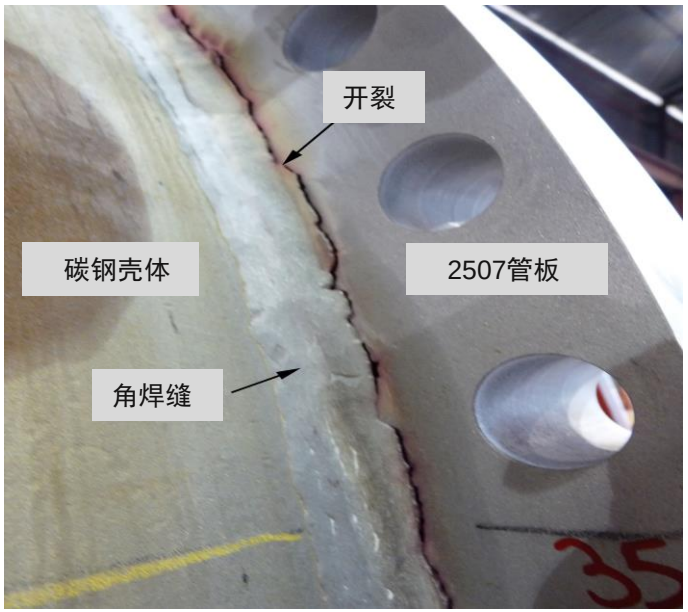
Isothermal precipitation kinetics of intermediates phases in duplex stainless steels

双相不锈钢 – 避免金属间相

Duplex grades. Avoiding intermetallic phases

- 2507管板与碳钢外壳
  2507 tube sheet joined to carbon steel shell
- 运行前，2507 HAZ出现裂纹
  Cracking in 2507 HAZ before operation began
- 母材发现σ相，与焊接无关
  Sigma phase found in base metal, unrelated to welding





2507管板失效是因为母材中有σ相析出Failed 2507 tube sheet due to sigma phase precipitation in 2507 base metal

双相不锈钢 – 避免金属间相
Duplex grades. Avoiding intermetallic phases

奥氏体/铁素体相平衡
Austenite/ferrite phase balance

相不平衡 Phase imbalance

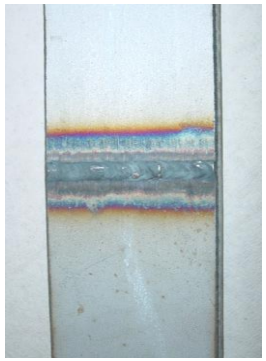
- 铁素体相占比高 High ferrite (> 70%):
  - 延展性差 Low ductility
  - 耐蚀性降低 Loss of corrosion resistance
  - 易发生氢脆 Susceptibility to hydrogen cracking
- 奥氏体相占比高 High austenite (> 80%):
  - 耐应力腐蚀性能差 Low SCC resistance
  - 强度低 Low strength

→ 避免不平衡 Avoid imbalance

双相不锈钢 – 避免金属间相

Duplex grades. Avoiding intermetallic phases

焊缝回火色 Presence of weld heat tint



- 焊缝回火色主要是铬氧化物
  Weld heat tint is mainly Cr oxide
- 回火色下面的合金贫铬
  Underlying alloy depleted of Cr
- 双相不锈钢，特别是经济型牌号，耐蚀性主要源于铬
  DSS, specially lean grades, get much of their corrosion resistance from Cr
- 回火色（或清除不当）会大大降低耐局部腐蚀性能
  Heat tint (or improperly removed heat tint) can substantially reduce resistance to localized corrosion
- 局部腐蚀选择性侵蚀奥氏体相或铁素体相，而且蔓延速度快。
  Localized corrosion of DSS usually selectively attacks either the austenite or ferrite phase, resulting in rapid propagation

→ 认真清除回火色 Remove heat tint carefully!

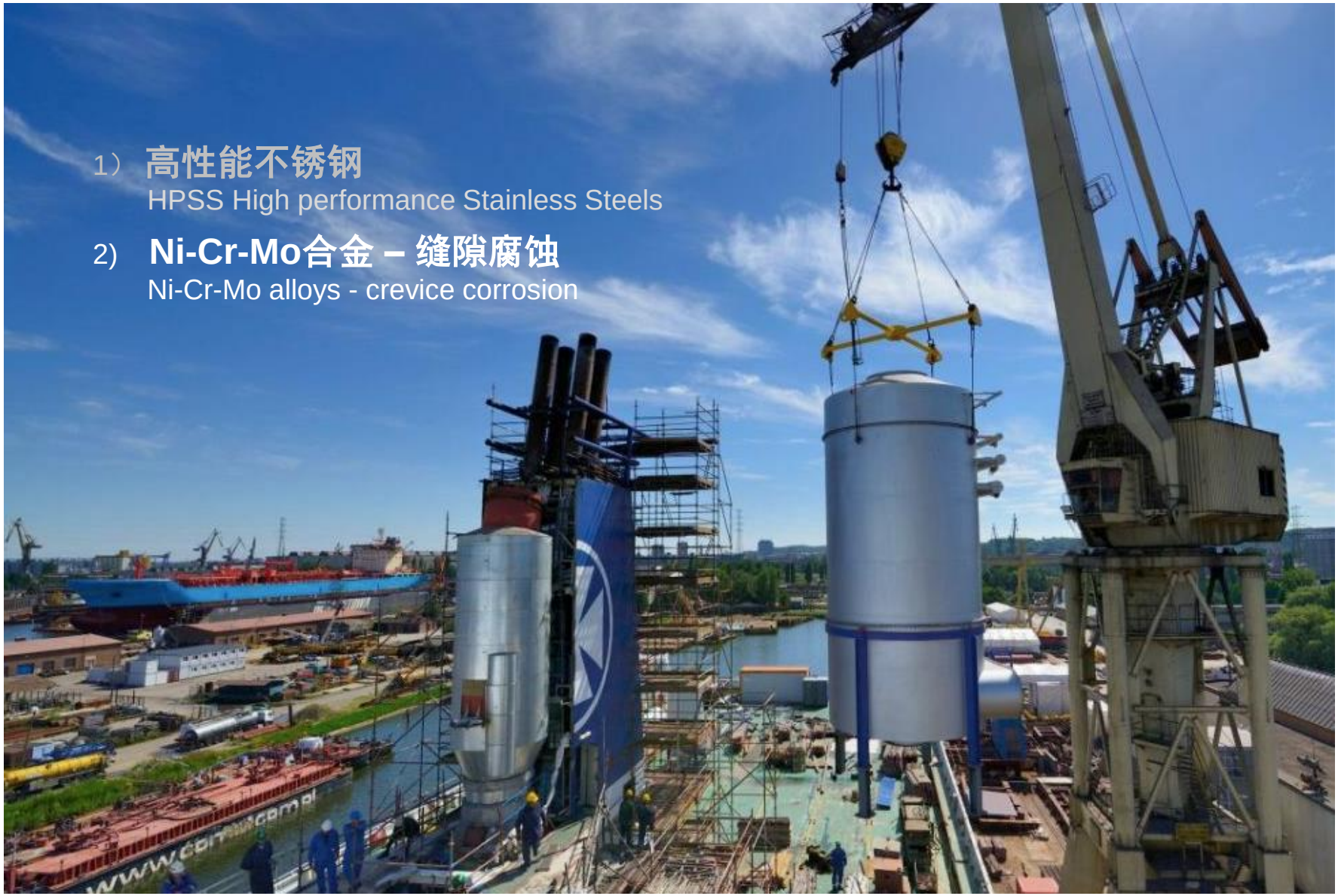
双相不锈钢 – 避免金属间相

Duplex grades. Avoiding intermetallic phases

激光切割 Laser-cutting

- 激光束精确聚焦
  Narrow focused laser beam
- 热量输入低
  Low heat inputs
- 冷却速度非常快
  Very rapid cooling rates
- 热影响区很窄且铁素体相占比高
  Very narrow HAZ with high ferrite contents
- 切口的耐蚀性下降
  As-cut edges can have reduced corrosion resistance

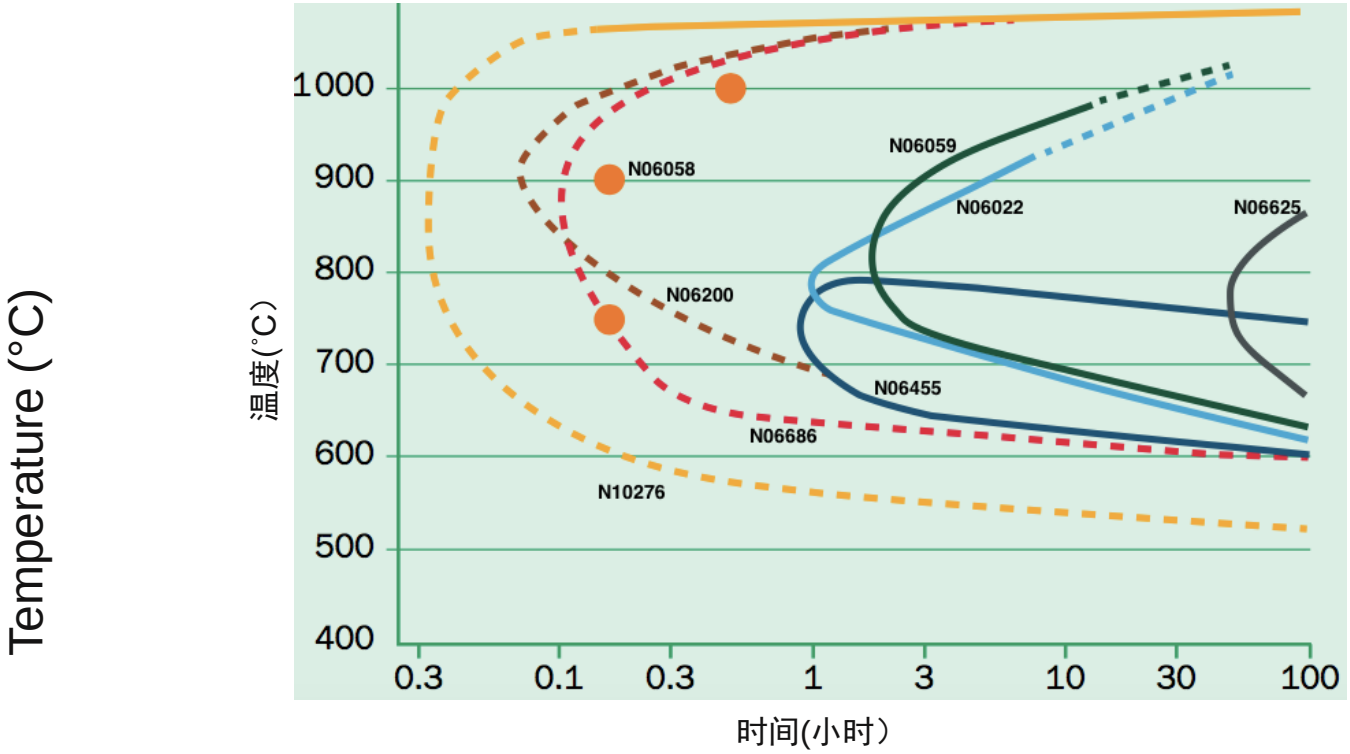
制作注意事项 Precautions for the fabrication



Ni-Cr-Mo合金 – 缝隙腐蚀

Ni-Cr-Mo alloys - crevice corrosion

Fabrication Quality



Ni-Cr-Mo合金 – 缝隙腐蚀

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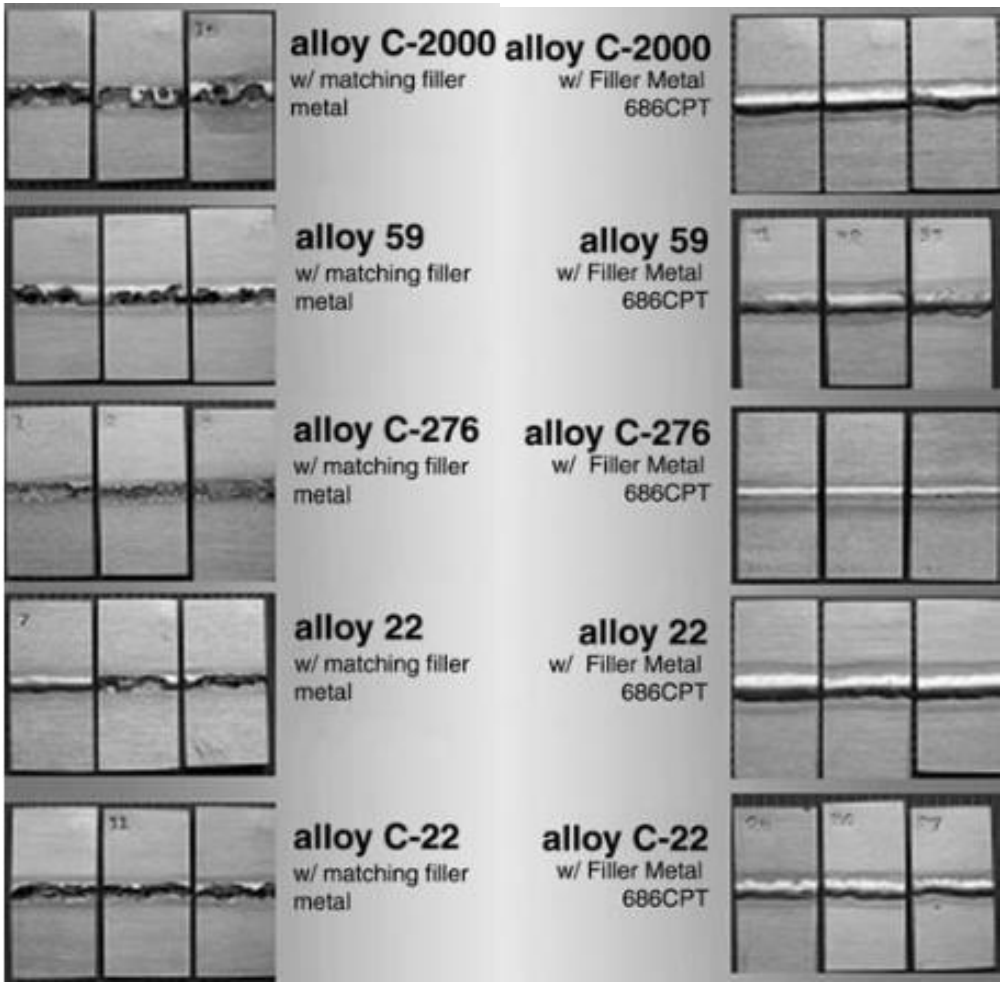


L. E. Shoemaker; J. R. Crum - Special Metals Corporation, Huntington, WV 25705 USA

试样在沸腾的green death 溶液中暴露72小时

Samples exposed in boiling (103°C) green death solution for 72 hours.

焊接高级耐蚀合金时，建议使用过匹配焊料

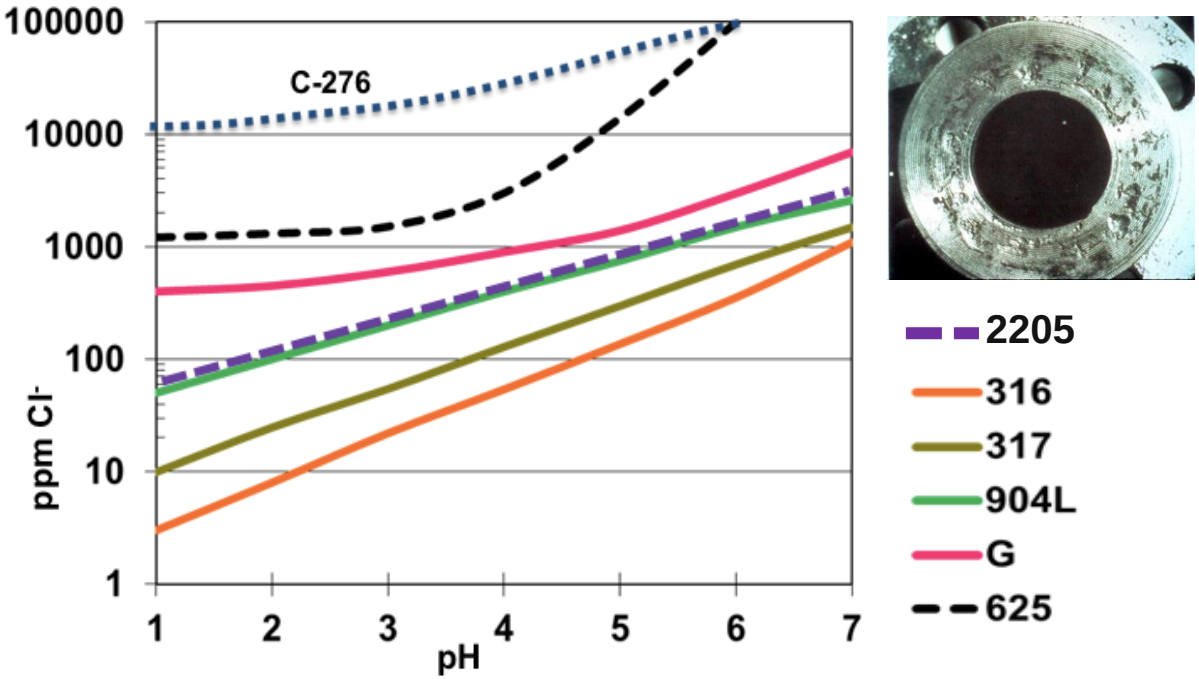
For joining all the advanced corrosion-resistant alloys using overmatching composition for welding products is highly recommendable

Ni-Cr-Mo合金 – 缝隙腐蚀

Ni-Cr-Mo alloys - crevice corrosion

pH值和氯化物对耐缝隙腐蚀性的影响

Effect of pH and Chlorides on Crevice Corrosion Resistance



但是该图（$T_{最大}$=60℃，中等氧化电位）未能准确描述高氧化条件下，特别是锰的存在金属表面形成缝隙的情况。

Graphs developed (based on a T=60oC max., moderate oxidizing potential) failed to accurately depict highly oxidizing conditions, especially with Mn present which formed crevices on the metal surfaces

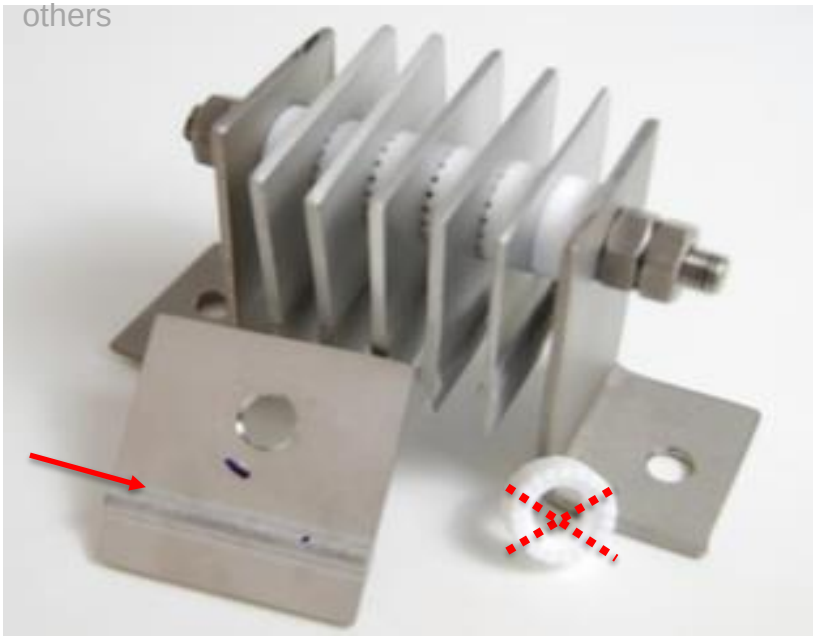
船用烟气洗涤器用合金的评定，焊接和缝隙的影响

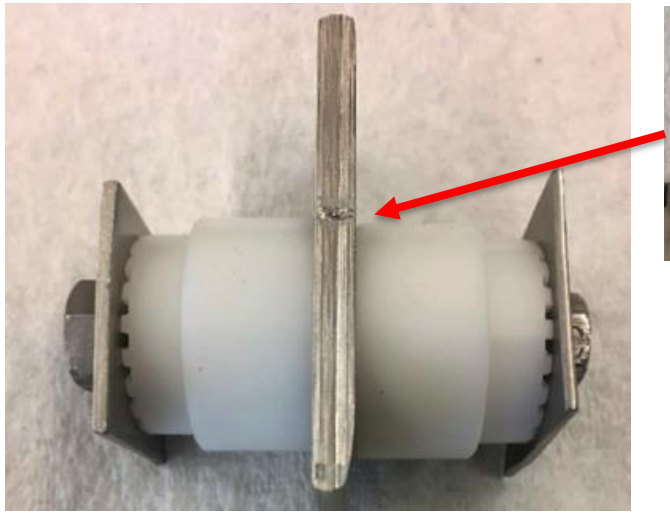
Evaluation of Alloys for marine exhaust scrubbers, effect of welding and crevice - 2018

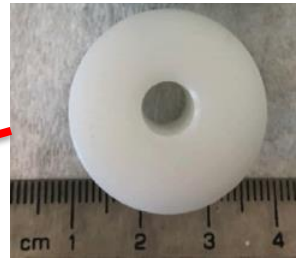
UNS	Cr	Ni	Mo	N	Cu	W
S31603	16.7	10.1	2.03	0.04	-	-
N08367	20.7	23.7	6.15	0.21	-	-
N08031	26.7	31.2	6.4	0.2	1.3	-
N10276	15.4	58.6	15.5	0.006	0.006	0.028
N06059	22.8	61.2	15.4	0.008	0.04	3.54

试样全部采用GMAW焊（氦-氩混合）。316L的填充金属为316LSi，其他材料的填充金属均为NiCr23-Mo16（类似于N06059）

All samples welded GMAW (helium-argon mix). Filler metal 316LSi for 316L and NiCr23-Mo16 (similar to N06059) for all the others







Source: Evaluation of Alloys for marine exhaust scrubbers, effect of welding and crevice – J. F. Grubb and Brien de Force – 2018 NACE Corrosion

船用烟气洗涤器用合金的评定，焊接和缝隙的影响

Evaluation of Alloys for marine exhaust scrubbers, effect of welding and crevice - 2018

在多种海洋洗涤器模拟环境中进行浸没腐蚀试验。80℃为与塔壁接触的洗涤液的温度上限。

Immersion corrosion tests were done in simulated marine scrubber environment, representing a wide range of conditions. 80 °C selected as upper limit of scrubber solution in contact with the wall.

Description	pH	Cl^- (ppm)	T (°C)
Simulated Scrubber Environment – Mild (crevice)	2	20,000	80
Simulated Scrubber Environment – Moderate (crevice)	2	60,000	80
Simulated Scrubber Environment – Moderate Severe	0.5	60,000	80
Simulated Scrubber Environment – Severe	0.5	110,000	80

使用缝隙试样（参考ASTM G48），促使温和和中等环境中发生缝隙腐蚀。

The crevice samples (Ref ASTM G48) were used with the attempt to promote crevice corrosion in the mild and moderate environments.

以下试验结果出自中等环境（ 168小时, 80 °C, 60.000 ppm 氯化物）

Next slides refer to the results after test in Moderate environment (168h, 80 °C, 60.000 ppm Chloride)

Source: Evaluation of Alloys for marine exhaust scrubbers, effect of welding and crevice – J. F. Grubb and Brien de Force – 2018 NACE Corrosion

船用烟气洗涤器用合金的评定，焊接和缝隙的影响

Evaluation of Alloys for marine exhaust scrubbers, effect of welding and crevice - 2018

模拟洗涤器环境 – 中等

Simulated scrubber environment - moderate

以2%钼为参照。表面浸蚀，轻微失重

2% Mo used only as reference. Surface etching, slight weight loss

Source: Evaluation of Alloys for marine exhaust scrubbers, effect of welding and crevice – J. F. Grubb and Brien de Force – 2018 NACE Corrosion

船用烟气洗涤器用合金的评定，焊接和缝隙的影响

Evaluation of Alloys for marine exhaust scrubbers, effect of welding and crevice - 2018

（上一张幻灯片）6%钼合金有表面侵蚀（没有明显的重量损失），合金31也如此，尽管它的铬含量为26%。

(previous slide) The 6% Mo Alloys show surface attack (without appreciable weight loss), even Alloy 31 in spite of its 26% Cr .

只有15%钼合金的表面浸蚀可忽略不计，而且没有明显的重量损失。

Only 15% Moly Alloys show negligible surface etching and no appreciable weight loss.

Source: Evaluation of Alloys for marine exhaust scrubbers, effect of welding and crevice – J. F. Grubb and Brien de Force – 2018 NACE Corrosion

INTERNATIONAL MOLYBDENUM ASSOCIATION
THE VOICE OF THE MOLYBDENUM INDUSTRY

结束语

- 船用洗涤器是极度恶劣环境中的敏感设备
  Marine Scrubbers are sensitive equipment sitting in a highly hostile environment
- 设计精度和制造质量是至关重要
  Design accuracy and Fabrication quality are vital factors
- 钼是选材的关键
  Moly is key in material selection

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谢谢