Why Stainless Steel Corrodes

The magazine "Nature" published two articles in the February 14th 2002 edition that are of interest to all specifiers, fabricators, users and if fact anyone involved with stainless steels. The leading article was a report of research work done at Imperial College of of Science, Technology and Medicine, by Mary P. Ryan and co-workers, entitled "Why stainless steel corrodes". There was also a "commentary" article by Roger C Newman of the Corrosion and Protection Centre, University of Manchester Institute of Science and Technology, entitled "Beyond the kitchen sink". The research at Imperial College described in Mary Ryan's article is of fundamental interest to all of us involved in promoting the understanding of stainless steels. Some of the discussion and conclusions were however re-reported in a number of "feature" articles in other publications through February and March, where the writers made what may be misleading statements on the corrosion resistance and processing of stainless steels.
These included: -

"Steel's fatal flaw found" - John Whitfield - Nature Science Update, 14th February
"A steely mystery comes to an end" - Fiona Harvey - Financial Times, 14th February
"UK scientists solve pitfalls in stainless steel" - Rob Coppinger - The Engineer, 15th February
"Stainless steel rust riddle is finally solved - Professional Engineering, 27th February
"Why it's the pits for stainless steel" - Materials World, March 2002

We will try to clarify some of the issues raised in this month's "Your questions answered"

The research at Imperial College involved analysing the chromium in a "316F" resulphurized sample across the boundaries between sulphide inclusions and the surrounding steel, using what seem to be reputable, modern micro-analysis techniques. They claim to show that over distances of 200 to 400 nanometres (0.2 μm - 0.4μm) into the metal, from sulphide inclusion edges, the chromium level falls from the "bulk" level of around 18% to around 10 atomic percent. Further analysis of some inclusions showed "outer rings" rich in chromium and manganese. A model of chromium migration from metal to sulphide inclusions during the steel and non-metallic solidification stages of steel-making is then postulated. They discuss the implications of this finding on localised pitting corrosion resistance in these chromium-depleted zones.
So far so good. I think we can identify this as similar to the mechanism accepted for intercrystalline corrosion (weld decay) following the formation of chromium carbides in standard carbon or un-stabilised austenitics during sensitisation heat treatments. On reading the article, the Imperial College team do not seem to have done any work themselves to prove their corrosion theory but have relied on surveys of other researcher's work to develop their discussion and conclusions. They acknowledge that a re-sulphurized steel type was used for the chromium scans so that there would be large number of inclusions available for analysis but go on to claim that localised corrosion in "low-sulphur" steels is always associated with sulphide inclusions. Other research is mentioned as noting that sulphide inclusions are "inactive as sites for stable corrosion initiation if they are sufficiently small" and that “in steels with this Cr (chromium) content" (shall we assume this to be around 18%) "that are completely free of inclusions pitting does not occur". Finally they seem to turn this round to make the claim "Other than this, there is no evidence that the mechanism of corrosion initiation at small inclusions is any different from that of large ones." - Getting confused?

Unfortunately the "commentary" articles mentioned developed these assertions with "popular" headlines and statements that could do unnecessary damage to the reputation of stainless steels, painstakingly built up over many years by researchers and industry professionals, including the members of the BSSA.

Roger Newman's article does clarify that the type of re-sulphurized steel used in the Imperial College research is used specifically where parts require "extensive machining" and that the sulphur levels in standard grades is normally in the range of 0.001-0.003%. He suggests that the lower the sulphide impurity, the better the corrosion resistance in "saline environments" and mentions the benefits of molybdenum alloy additions. He goes on to speculate that "unconventional" heat treatments or alloy additions of titanium to "tie up" the sulphur might be used to improve the corrosion resistance of stainless steels. There is no further explanation of how these proposed mechanisms would work. The article in "The Engineer", based on comments from Mary Ryan, suggests heat treatments "after manufacture" (steel-making?) as a method believed to replenish chromium levels at the surface by "heating and rapid cooling". Again there is no explanation whether this applies only to re-sulphurized steels or all grades or how the mechanism is supposed to work.

The Financial Times article is very confusing as it suggests that "chloride ions in the water used in the steel-making process"…"dissolve the unprotected steel" during pitting corrosion. The original work does not suggest this and, from my knowledge of stainless steel-making, this is an absurd statement.

Roger Newman's article finally suggests that "the technology for treating stainless steel surfaces" should be reassessed (i.e. mill and mechanically polished surface finishes in particular) as little is known about the behaviour of near surface sulphides during these processes. There is no explanation or justification for making this suggestion, based on the findings reported by Mary Ryan's team. The "Nature" feature by John Whitfield reports that Roger Newman may be suggesting post mechanical finishing heat treatments to re-diffuse chromium to the surface of the finished steel, but adds "manufacturers might baulk at the cost of adding an extra step to the production process". It appears that Roger Newman's suggestions may have been misquoted or his comments at least taken out of context. There is no indication whether this proposal applies only to re-sulphurized steel types or all stainless steels, i.e. the bulk of stainless steel produced with low sulphur levels and hence low volume fractions of sulphide inclusions. There seems to be no justification for this concluding remark made by John Whitfield.

The threat that pitting corrosion poses to stainless steels has been known for many years.
It is in our interests in the BSSA to gain more understanding about corrosion mechanisms and we should always welcome further scientifically proven research work.
Conclusions and recommendations for avoiding or minimising corrosion must however always be based on carefully developed ideas with justifiable, practical recommendations, specific to particular grades and in the context of specific service environments.

We acknowledge that stainless steels are not immune to corrosion in all circumstances, but always assert that stainless steels, correctly selected for specific service environments, properly designed, fabricated and finished should not suffer from unacceptable pitting corrosion.

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