Material Trends for High Purity and Sanitary Applications

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For several years stainless steel has been the workhorse processors have used in tough corrosive environments and for the most part, it has performed well. In recent years however, when it comes to new installations or even repairs to existing process lines, today's stainless steel doesn't perform as well in the same application as stainless steel of years past. Additionally, with the advent of newer buffer solutions in the pharmaceutical industry we are experiencing higher than ever chloride levels which attack stainless steel causing pitting and crevice corrosion.

As with all industries, imports, competitive markets and technological advances have enabled and even forced steel manufacturers to become more competitive in the steel making process. The most significant of these advancements impacting the steel industry was realized nearly 40 years ago with the introduction of argon-oxygen-decarburization (AOD) refining. The use of AOD allows the extensive use of scrap metal. In fact, some heats are nearly all remelted scrap metal. The only disadvantage is a continual build-up of non-specified tramp elements like copper, boron and calcium. The AOD process allows precise gas manipulation to achieve the desired result and refines stainless steel by gradually replacing oxygen by means of blowing argon through the molten metal to eliminate impurities.

The American Society for Testing and Materials (ASTM) specification shows the chemical composition of any alloy in ranges with a minimum and maximum allowable limit to meet the requirements for the specific alloy. For example, the chemical composition for 316L stainless is as follows.

316L	Chromium	Nickel	Molybdenum	Carbon	Iron
Minimum	16%	10%	2%		
Maximum	18%	14%	3%	0.035%	Balance

Today, when alloying 316L stainless steel the AOD process allows precise control of alloying elements, enabling the mills to make a product to an exact chemical composition. This also allows the elements to be controlled to the minimum range allowed for the specification. Compared to decades past when alloying 316L, the amounts of alloying elements were added with little control and often pushed or exceeded the upper limits of the maximum requirements. The resulting steel was a product with corrosion resistant properties superior to 316L stainless steel that is manufactured by using today's methods. Today we see melts of steel meet the requirements of the specification on the low end, resulting in the overall mean corrosion resistance of the material trending downward. If a higher alloyed, but within-grade, 316L composition is desired, it typically requires a special order of a full heat of material. Due to the cost or purchasing a complete melt, it is often more practical to specify a more corrosion resistant grade such as 904L, duplex stainless steel or a 6% Mo grade to obtain small quantities than to special order an enhanced 316L composition.

Determining the corrosion resistance of any alloy is always a challenging task. Varying service environments, aggressive cleaning and sterilization practices, and even multiple product forms of materials used in equipment fabrication can have a negative impact on corrosion resistance of materials. Because of these ever-changing conditions, the best corrosion data available is often the service history of the system itself. When choosing the correct materials of construction, it is recommended that a qualified Materials Engineer be consulted for evaluating the solutions, compounds and operating conditions the system will be exposed to. The most widely accepted materials of construction beyond 316L stainless steel in high purity and sanitary applications are the super-austenitic, nickel, and duplex alloys. These alloys can vary in their chemical make-up resulting in different levels of performance in certain corrosive or acidic environments. Table MM-2.1-1 in the current edition of the ASME BPE Standard identifies materials acceptable for use in the Biopharmaceutical industries that have been proven they can meet the requirements of welding and surface finishes listed within the Standard. Of these materials listed, this paper is going focus on Type 316L austenitic, superaustenitic stainless steels 904L, Ultra6XN, AL-6XN® and nickel alloys C-22® and Alloy 22.

ASTM Composition of Wrought Steels

UNS	Alloy	EN	C	Mn*	Cr	Ni	Mo	N*	Cu	PREN
S31603	316L	1.4404	0.030	2.00	16.00-18.00	10.00-14.00	2.00-3.00	0.10	…	24
N08904	904L	1.4539	0.02	2.00	19.0-23.0	23.9-28.0	4.0-5.0	-	1.0-2.0	36
N08367 N08926	Ultra 6xn	1.4529	0.02	2.00	19.0-21.0	24.0-26.0	6.0-7.0	0.15-0.25	0.75	45
N08367	AL-6XN®	-	0.03	2.00	20.0-22.0	23.5-25.5	6.0-7.0	0.18-0.25	0.75	45.2
N06022	C-22®	2.4602	0.01		22	56	13		0.5	68
N06022	Alloy 22	2.4602	0.015		22	56	13		0.5	68

*Maximum
Note: Sulfur is limited to 0.030 max and Phosphorous to 0.045

When comparing alloys for corrosive environments, the most important elements of the materials chemistry for corrosion resistance is Chromium, Molybdenum, Nickel and Iron. None of these listed elements alone are magical in preventing corrosion but alloyed correctly and manufactured properly, can improve corrosion resistance and the life expectancy of a high purity system.

- Chromium – Cr is a key component of stainless steel that accounts for its passive nature. Chromium significantly improves corrosion resistance when the composition contains a minimum of 10.5%. When at or above these levels, an adherent and insoluble surface film, known as the passive film, is instantaneously formed that prevents diffusion of oxygen into the surface thus prevents oxidation of the iron in 316L stainless steel. Chromium is also the weak link in stainless steel when in contact with chlorides by reacting with the chromium oxide in the passive layer to form chromium chloride, which is very soluble. This leaves a layer of iron and iron-nickel on the surface, an active film which will allow the stainless steel to corrode and the metal to be consumed.

- Molybdenum – Mo increases the resistance to localized corrosion in the forms of pitting and crevice corrosion. The higher the molybdenum content, the better the corrosion resistance to higher chloride levels by enhancing the passive film, making it stronger and helping it to re-form quickly if it is disrupted by chlorides.

- Nickel – Ni is an alloying element critical to stainless steels and results in the formation of the austenitic structure that increases strength, impact strength and toughness, while also improving resistance to oxidization and corrosion. It also increases toughness at low "cryogenic" temperatures. Nickel has no direct impact in the formation of the passive layer, but it does offer improvement in resistance to acid attack.

Another alloying element that has a positive impact and found in 316L, Ultra 6XN and AL-6XN® is Nitrogen-N, which increases the austenitic stability of stainless steels and improves yield strengths in low carbon grades of steel containing less than 0.03%. It can also enhance resistance to localized pitting and intergranular corrosion.

A guide to the corrosion resistance of alloy can be found in the calculation of its Pitting Resistance Equivalency Number (PREN). The chemical composition of the alloy along with this formula (Cr + 3.3Mo + 16N=PREN) will result in a number ranking the alloy. The higher the number, the more resistant the alloy is to localized corrosion. PREN's can be found in the materials table above.

Those alloys containing 6% molybdenum content may require special fabrication methods beyond what is generally found in 316L stainless steel systems. However, they are common place and manufacturing practices are available to guide fabricators and suppliers. All the alloys listed in the table above are available in common sizes found in most sanitary designs and product forms such as tubing, fittings and valves.

For information regarding pricing and specifics of fabrication please contact the author.

AL-6XN® in a registered trademark of Allegheny Technologies Inc.

C-22® is a registered trademark of Haynes International Inc.

About the Author:

Ken Kimbrel is Product Manager - Special Alloys for VNE Corporation in Janesville, WI. He is responsible for specialty alloy sales, market planning, process and material evaluation in corrosive environments. He attended Tulsa Community College and has an extensive background in engineering, equipment manufacturing, and is a NACE International Board-Certified Corrosion Technician. His expertise includes corrosion evaluation, material selection, surface finish evaluation, and rouge remediation.

Ken is the current Chair of the ASME BPE. He has served as inaugural Chair of Subcommittee on Metallic Materials and as past Chair of the Surface Finish Subcommittee. He is a member of the Subcommittees on Accreditation, the Standards committee, Executive committee and author of several technical papers.

He is a member of the International Society for Pharmaceutical Engineering (ISPE), ASM International (ASM), the International Metallographic Society (IMS), the National Association of Corrosion Engineers (NACE).

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