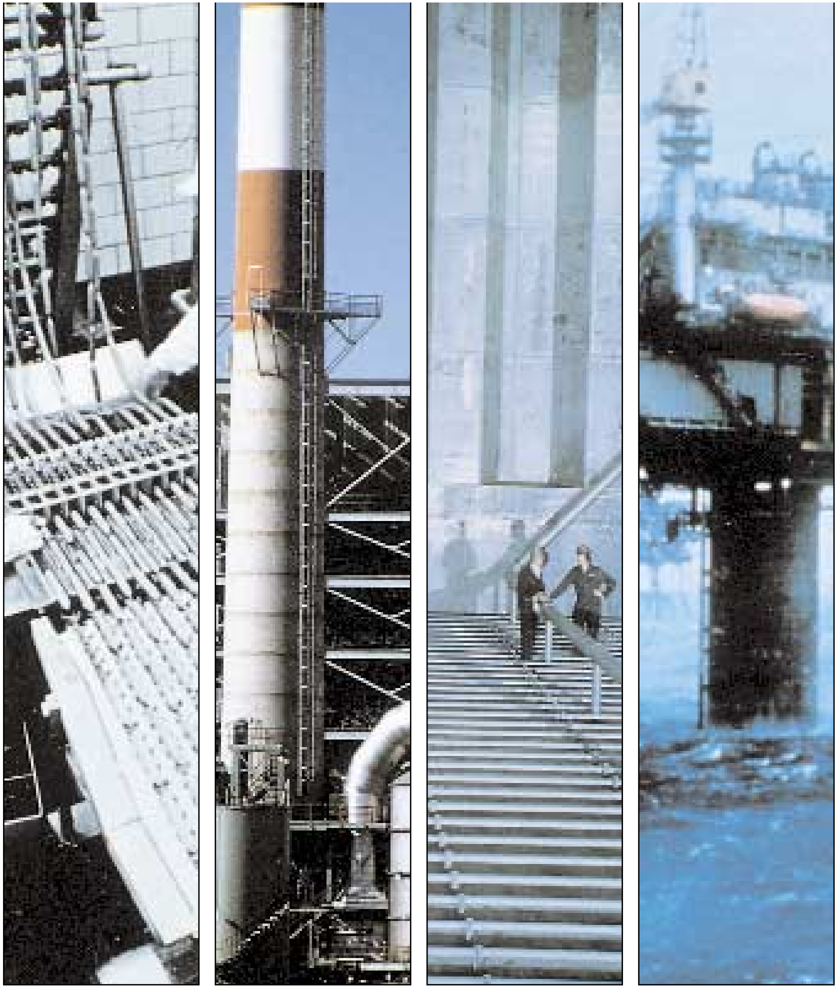

THE EVOLUTION OF HIGH PERFORMANCE STAINLESS STEELS

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TABLE 1.
NOMINAL COMPOSITIONS (WT. PCT.)

UNS Number	Proposed EN 10027 Number	Alloy Name	Cr	Ni	Mo	Cu	N	Other
Standard Austenitic Stainless Steels								
S30403	1.4307	Type 304L	18	8	–	–	–	–
S31603	1.4404	Type 316L	16	11	2	–	–	–
N08020	–	Alloy 20	20	34	2.2	3.5	–	Cb
S31703	1.4438	Type 317L	18	12	3	–	–	–
High Performance Austenitic Stainless Steels								
–	–	Alloy 24	24	17	4	–	0.40	6 Mn
S31725	–	317LM	18	13	4.3	–	–	–
S31726	1.4439	317LMN	17	14	4.25	–	0.15	–
N08904	1.4539	904L	20	25	4.5	1.5	–	–
S34565	–	4565 S	24	17	4.5	–	0.50	6 Mn
N08932	1.4537	UR SB8 (1)	25	25	5	1.5	0.20	–
S31254	1.4547	254 SMO (2)	20	18	6	0.75	0.20	–
N08367	–	AL-6XN (3)	20	24	6	–	0.20	–
N08926	1.4529	1925hMo (4) / 25-6MO (5)	20	25	6	1	0.20	–
–	–	Polarit 778 (6)	20	22	6	0.75	0.20	–
N08026	–	20Mo-6 (7)	23	34	6	3	0.12	–
N08031	–	Alloy 31	27	31	6	1.2	0.20	–
S32654	–	654 SMO (2)	24	22	7.3	0.50	0.50	3 Mn
Second Generation Duplex Stainless Steels								
S32304	1.4362	2304	23	4	–	–	0.10	–
S32950	1.4460	7-Mo PLUS (7)	26.5	4.8	1.5	–	0.20	–
S31803	1.4462	2205	22	5	3	–	0.02	–
S32550	1.4507	Ferralium 255 (8)	25	6	3	2	0.20	–
S31260	–	DP-3 (9)	25	7	3	0.5	0.15	0.3 W
S37260	1.4501	Zeron 100 (10)	25	7	3.6	0.75	0.25	0.75 W
–	1.4507	UR52N+ (1)	25	6	3.8	1.5	0.25	–
S32750	1.4410	2507	25	7	4	–	0.25	–
High Performance Ferritic Stainless Steels								
S44400	1.4521	Type 444 (18Cr-2Mo)	18	–	2	–	–	Ti, Nb
S44627	–	E-BRITE 26-1 (3)	26	–	1	–	–	Nb
–	–	29Cr-3Mo (11)	29	–	3	–	–	0.4 Ti
S44660	–	SEA-CURE (12)	27.5	2	3.5	–	–	0.4 Ti
S44735	1.4592	AL 29-4C (3) / 290 Mo (11)	29	–	4	–	–	0.4 Ti

(1) Trademark of Creusot-Loire Industrie
(2) Trademark of Avesta Sheffield AB
(3) Trademark of Allegheny Ludlum Corp.
(4) Trademark of Krupp-VDM
(5) Trademark of the INCO family of companies
(6) Trademark of Outokumpu Oy
(7) Trademark of Carpenter Technology Corp.
(8) Trademark of Langley Alloys Ltd.
(9) Trademark of Sumitomo Metals
(10) Trademark of Weir Materials Ltd.
(11) Trademark of Vallourec
(12) Trademark of Crucible Materials Corp.

STAINLESS STEEL 93

In the most recent years, there has been an annual international conference on stainless steels. **Innovation Stainless Steel**, the Stainless Steel 93 conference, was held in Florence, Italy, October 11-14, 1993. As suggested by its title, it focused on both the results of innovations in the stainless steel industry and on the process of innovation itself. The Conference was sponsored by the Associazione Italiana de Metallurgia, under the auspices of the Commission of the European Communities and the Nickel Development Institute. It would be difficult to imagine a place of richer cultural heritage or a more hospitable host. For those who could not attend, we must say that you missed a wonderful personal experience. We cannot hope to adequately describe the delight of Florence, but we will offer here a brief review of some of the technical discussions.

IMOA was pleased to sponsor a paper (1). Written by Davison and Redmond, both formerly with the Climax Molybdenum Company in the United States, it examined the processes of innovation and evolution that have brought so many new grades of stainless steel to commercial significance in the twenty-five years since the introduction of argon oxygen decarburization (AOD) refining. This paper, The Evolution of High Performance Stainless Steels, is reprinted in this brochure.

For this summary we have chosen to focus on just four major themes of the Conference:

1. Role of nitrogen in austenitic stainless steels;
2. Maturing of the second generation of duplex stainless steels;
3. Role of stainless steel in everyday life; and
4. Public education on stainless steel.

ROLE OF NITROGEN

One feature of the AOD and similar refining vessels that was not fully appreciated in the first decade of application was the ease of introduction and precise control of nitrogen as an alloy element in stainless steel. Initially considered only as an inexpensive austenitizer, nitrogen is now appreciated for its contributions to strength, corrosion resistance, and phase stability in austenitic stainless steel with high chromium and molybdenum. As in the past, the Swiss Federal Institute of Technology made excellent contributions, both in defining the potential for future developments and in facilitating practical applications of the high nitrogen materials. Speidel, always the enthusiastic advocate for the high nitrogen technology, discussed corrosion resistant tool steels of remarkable nitrogen content produced by powder metallurgy and by high pressure electroslag remelting (2). His associates at the Institute demonstrated the comprehensive approach being followed. Uggowitzer presented a theoretical d-shell electron theory justification for the effects of nitrogen (3). Rechsteiner showed how melting under high pressure nitrogen enables practical production of austenitic stainless steels with up to 1.1% nitrogen (2). Paulus addressed the difficulties of processing these high strength materials on conventional equipment with an evaluation of warm processing techniques (4).

Only a few years ago the idea of commercialization of a 0.5% nitrogen austenitic stainless steel would have been thought radical, far in the future. But Wallén of Avesta Sheffield AB in Sweden reported on the new 654 SMO austenitic stainless steel with 24Cr-22Ni-7.3Mo-0.5N (5). Produced in conventional AOD and continuous cast in 70-ton commercial heats, this astonishing austenitic stainless steel has corrosion resistance approaching that of the nickel-base C alloys, together with substantially higher strength. (If we called the 6Mo-0.2N austenitic stainless steels the "super austenitics", what must we call this new grade?)

With the high cost of alloy development, it is encouraging that the evolution of these new grades is not wholly empirical. Theoretical studies of the thermodynamics of high nitrogen steels in advance of the production trials have greatly shortened the time for development. For example, Foct of the Université de Lille in France discussed the thermodynamics of high nitrogen steels with the goal of reducing the practical limitations of production (6).

In addition to the quantum leap to 0.5% N austenitic stainless steels, this is also the logical broadening to the range of products at the 0.2% N level. White, of Krupp VDM in Germany, reported on Nicrofer 3127, a high chromium 6% Mo grade with high nickel and copper, designed for high chloride acid streams, especially sulfuric and phosphoric acids (7).

One focus of **Innovation Stainless Steel** was the recognition of the series of metallurgical and commercial barriers that must be overcome to move a research concept to practical application. One aspect of this process is the need for a full range of welding practices to be developed for each new grade, including conventional high deposition rate welding, to assure that the new grade is economically competitive. Skirfors, speaking for the Royal Institute of Technology and

Sandvik Steel AB of Sweden, reviewed the success achieved in welding the highly alloyed austenitic stainless steels by the submerged arc process, overcoming limitations of hot cracking that were previously assumed to apply to these grades with austenitic solidification (8). A remarkable range of fillers, fluxes, and techniques have moved the super austenitics from special grades to standard materials of construction.

DUPLEX STAINLESS STEELS

There have been many conferences dedicated solely to duplex stainless steel technology. **Innovation Stainless Steel** did not try to compete with the intensity and detail of those conferences, but the duplex stainless papers of Florence do mark the progress of the duplex stainless development. In only one decade, the second generation of duplex stainless steels has become a complex family of great commercial significance and a comprehensive range of applications. Charles of Creusot-Loire Industrie of France gave an excellent survey of the evolution of the family of duplex grades (9). The second generation is characterized by higher nitrogen contents, so it is no surprise that the duplex stainless steel development has proceeded simultaneously with that of the new austenitic grades.

Gooch, speaking for The Welding Institute of the United Kingdom, showed the extent of their commercial acceptance of the duplex grades (10). It is clear that good welds can now be made by a range of welding processes. What is occurring now is the standardization of procedures and qualifications, and the education of both fabricators and users, to permit the general use of the new and distinctive family of stainless steels.

Several technically excellent papers demonstrated the quality of the increased understanding of duplex stainless steel welding and transformations. Nilsson, presenting a joint research effort of Sandvik Steel AB, Esab AB, and Avesta Sheffield AB of Sweden, showed the formation of secondary austenite in duplex welds, and with thermodynamic modeling and direct observations, explained the susceptibility of secondary austenite to pitting attack (11). Hertzman of the Swedish Institute for Metals Research showed that the various stainless steels conform to theoretical models for phase transformations, and that thereby the models are useful for predicting metal behavior (12).

Detailed analyses of hot working behavior of 2304 and 2205 stainless steels were provided by Barteri (13), of Centro Sviluppo Materiali of Italy, and by Paúl (14), of Acerinox of Spain. Even though duplex stainless steel was not an announced primary focus of **Innovation Stainless Steel**, it is indicative of the worldwide development of stainless steels that corrosion resistance, processing, welding, and applications of duplex grades were the subject of papers from Sweden, Korea, Belgium, France, Italy, Germany, Japan, Spain, Finland, and the United Kingdom.

CONSUMER APPLICATIONS

With all of the discussion of super austenitics and super duplexes, one might think that stainless steels are only for the most corrosive of applications; however, **Innovation Stainless Steel** also addressed the versatility of stainless steels in everyday life in food handling, automotive applications, architecture, and pollution control.

Stainless steels have for years been the standard by which all other materials have been judged for hygienic applications. Remarkably, some questions have been raised in this area as all materials are being subjected to review. The industry must view this situation in a positive way, that although costly, these programs are an opportunity to demonstrate and quantify the superiority of stainless steels in these applications.

Food applications, with a focus on the safety of stainless steel through non-interaction with the product and with ease of complete cleaning, were presented by Flint speaking for the Nickel Development Institute in the United Kingdom (15). Fischer (16), of Blanco GmbH of Germany, and Tupholme (17), speaking for British Steel Technical and Avesta Sheffield Ltd. of the United Kingdom, showed the thoroughness of this program to demonstrate the safety of stainless steels.

Automotive applications of stainless steel have become a substantial commercial significance, not just for the catalytic converters to control exhaust emissions, but also for the whole exhaust systems to provide the economical reliability and durability demanded by the consumer. This application was covered by several speakers, including Rutherford (18), of Allegheny Ludlum Corporation of the United States, and by Pauly (19), of Informationsstelle Edelstahl Rostfrei of Germany. The comments of these speakers on the role of stainless steels in flue gas desulfurization were expanded upon by the discussion of life cycle costing for high molybdenum stainless steels in this application as presented by Plant, of the Nickel Development Institute in the United Kingdom (20).
For lack of space in this discussion, we must make a general recommendation that the reader seek out the

papers in the Proceedings of **Innovation Stainless Steel** on architectural applications, the use of 12% Cr low maintenance steels, and on life cycle costing of stainless steel equipment.

PUBLIC AWARENESS OF STAINLESS STEEL

One disturbing trend in stainless steel development over the last decade has been the curtailing, in the name of reduced costs, of many of the research and development programs and the programs of industry associations for public education on stainless steels. This environment makes the unique effort of Mexinox in Mexico all the more praiseworthy (21). Aimed at building awareness of stainless steels, both in function and metallurgy, their program begins at the grade school level. With a well conceived package of educational comic books, puzzles, and games, "Superinox, un nuevo heroe" conveys stainless steel technology in a way that is accurate and fun. Each alloy element has its own character in the comic strip. We at IMOA are particularly appreciative of the charming señorita "Moly", and her good influence on the hero. This program deserves commendation for conveying the true spirit of **Innovation Stainless Steel**.

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ABSTRACT

This paper reviews the evolution of stainless steel technology in the ferritic, austenitic, and duplex stainless steel families of grades, the technology of their recent advances, their applications, their technical limitations, and the prospects for further evolution.

KEYWORDS

Argon-oxygen decarburization, vacuum oxygen decarburization, ferritic stainless steels, austenitic stainless steels, duplex stainless steels, nitrogen alloying.

INTRODUCTION

The evolution of high performance stainless steels is a race between the increasing needs of the end users on the one hand and the improvement of stainless steelmaking capabilities on the other hand. During the last two decades there has been a rapid and continuing escalation in both needs and capabilities.

On the user side, there have been two major factors: government mandated requirements and increased competitive pressures. Although controlling environmental pollution and minimizing safety risks are common sense, government legal and regulatory restrictions on activities of all companies assure that companies can pursue socially responsible programs without loss of competitive advantage. At the same time, there has been an intensification of the worldwide competitive pressures for production efficiency and for the avoidance of unscheduled maintenance. A better understanding of the principles of life cycle costing and an appreciation of the risks of failures in the terms of lost production, personnel safety, and social responsibility have led to greater reliance on materials of superior performance and durability. Stainless steels figure prominently in meeting these needs.

On the stainless steel production side, the introduction of new refining technology, most notably the argon–oxygen decarburization (AOD) and vacuum–oxygen decarburization (VOD) in the early 1970s, led to the development of new grades within virtually all classes of stainless steel (1). These refining methods allowed more economical production of standard grades through the use of scrap and less expensive starting materials and through more precise control of alloy element additions, thereby making all stainless steels more attractive to the users. The new processes allowed conventional processing of steels containing higher chromium and molybdenum levels through the removal of tramp elements that caused breakup in hot rolling. Finally, these processing systems have opened the door to the use of nitrogen as an intentional and precisely controlled alloying addition, the basis of much of the new stainless steel technology in recent years.

FERRITIC STAINLESS STEELS

During the 1970s there was a great amount of technical development effort and discussion of the use of the new refining methods to overcome the practical limitations of ferritic stainless steels. These grades were difficult to produce in thicknesses heavier than moderate gauge sheet, and they were difficult to weld with reliable results at the levels of interstitial elements, particularly carbon and nitrogen, that were economically producible in conventional production equipment.

Application of AOD and VOD technology to ferritic stainless steels led to a series of grades, usually named by their Cr-Mo or Cr-Mo-Ni contents, as shown in Table 1. (Trademarks and commonly used names of the proprietary grades are attributed to producers in Table 1, but not in the text.) The economic justification based on the savings on nickel content proved illusory when the production difficulties were taken into account. However, the technical advantages, particularly their resistance to chloride stress corrosion cracking (SCC) and to chloride pitting and crevice attack, made these grades attractive, even at prices higher than the austenitics, for specialized applications as shown in **Figure 1.** Applications of this sort may be found for 18Cr-2Mo (Type 444, UNS S44400) in food processing, such as cooking equipment and hot water piping where the virtual immunity to SCC is of great value for long service life and personnel safety. The use of this and similar grades has been especially successful in Japan in solar hot water systems, domestic hot water heating, and heat transfer equipment in chemical and petrochemical processing (2).

Several ferritic stainless steels were developed especially for sea water condenser tubing, typically those grades with a combination of greater than 26% Cr and 3% Mo. Several of these grades used 2 to 4% Ni to provide increased toughness and ease of production and fabrication. This nickel addition eliminated the immunity of the ferritic grades to SCC in boiling 42% $MgCl_2$, the most generally accepted criterion of SCC resistance at that time. However, all of the newer ferritic stainless steels do pass the boiling 25% NaCl test and the "wick test" for resistance to SCC. All of the higher alloyed grades, sometimes grouped together as the "sea water ferritics", for example, SEA-CURE (UNS S44660), AL 29-4C (UNS S44735), and 290 Mo (UNS S44735), have provided excellent field performance in terms of pitting resistance and SCC resistance, with over 9.5 million meters of condenser tubing currently in service (3). However, these grades have encountered a problem in service attributed to hydrogen embrittlement resulting from inadequate control of cathodic protection systems for tubesheets and water boxes. Concern over this practical problem has restrained use of the sea water ferritics.

In addition to sea water applications, AL 29-4C has been used extensively for condensing heat exchangers in high efficiency, gas-fired, residential furnaces where the acid chloride condensate caused pitting attack in austenitic and ferritic grades with lower alloy content. **Figure 2** shows an example of such a device.

The prospects for further evolution of stainless production technology to overcome the limitations of the ferritic stainless steels are not promising. Material with levels of carbon and nitrogen substantially below the levels commercially achievable do not eliminate the problems with toughness, production, and welding of the ferritic stainless steels. Furthermore, the new duplex

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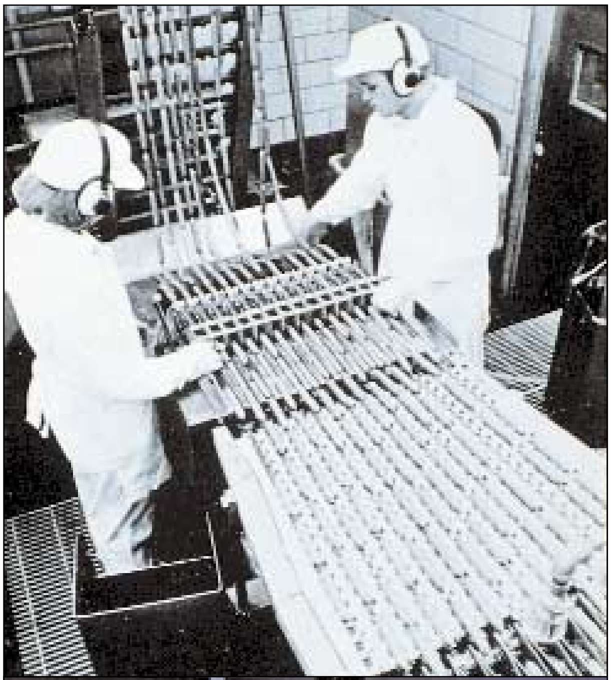

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stainless steels which trade a slightly higher alloy cost for substantially improved toughness, production, and fabrication characteristics are a formidable economic competitor for the ferritic grades. Nevertheless, there are proven applications where the outstanding performance of the new ferritic stainless steels outweighs their limitations.

AUSTENITIC STAINLESS STEELS

The impact of the new refining methods on austenitic stainless steels was large and pervasive. The ability to nearly double throughput of existing facilities by the relatively small capital investment in AOD equipment, with the electric furnaces dedicated primarily to initial melting, made the investment possible. The great reduction in total melt cost through the elimination of the need for pre-refinement of alloy metal additions made the investment inevitable. As a result, the standard stainless steels have become less expensive relative to other materials alternatives through this whole period.

Prior to introduction of the AOD, production of an austenitic stainless steel with greater than 18% Cr and 3% Mo was difficult and expensive because tramp elements caused hot cracking during initial slab breakdown and subsequent hot rolling. Even the common 316 was sensitive to these elements, reducing product yield. The AOD facilitates desulfurization, leading to a lower sulfur level, and permitting further treatment to levels of 0.001% or lower in standard production. The tramp metal impurities responsible for hot cracking through formation of low melting eutectics are also reduced. Consequently, production yields of 316 and 317 are increased and the way is opened to higher alloy levels.

The first step in the sequence of new grades was quite logically to increase molybdenum to the 4-5% range, with chromium at 20%, with increased nickel to maintain the austenitic structure. Most notable of these efforts are 317LM (UNS S31725) and Alloy 904L (UNS N08904), developed for flue gas desulfurization scrubbers and for chloride-contaminated sulfuric acid streams, respectively. These alloys have performed well, with Alloy 904L being especially successful in the sulfuric acid and phosphate industries. However, further extension of this approach of balanced additions of molybdenum and nickel runs into a significant technical barrier. At molybdenum levels above about 4.5%, there is an increasingly rapid tendency for formation of intermetallic phases, especially sigma phase, limiting section thickness and weldability (4). This effect was demonstrated by the success of Allegheny Ludlum AL-6X steel (UNS N08366) as light gauge condenser tubing, beginning in the early 1970s, competing with and eventually dominating the sea water ferritics in this application. However, AL-6X was not suitable for heavy sheet and plate applications because the formation of sigma phase could not be suppressed after heat treatment, and certainly not after field welding.

This technical limitation would have blocked further development of the austenitic stainless steels except for the discovery of the favorable effects of nitrogen. Nitrogen was originally used in AOD production as a method of reducing both nickel and argon costs. It was found that nitrogen in the injected gas would readily enter the steel and could be controlled very accurately. The nitrogen was not only an economical and highly effective austenitizer, it also provided significant increases in strength and chloride pitting and crevice corrosion resistance. But most importantly for the further evolution of high performance stainless steels, nitrogen effectively delays the formation of sigma and other intermetallic phases.

In the late 1970s Avesta 254 SMO (UNS S31254) stainless steel demonstrated that a nitrogen addition of about 0.2% permits the production of a 6% Mo austenitic stainless steel over a full range of section thicknesses and with excellent response to most types of welding (5). Other 6% Mo grades subsequently followed this nitrogen alloying approach, as shown in Table 1. The higher nickel in these other grades is attributable less to any technical necessity than to the path of historical development and the need to avoid conflict with patents of previously developed grades.

In the approximately fifteen years since the nitrogen-alloyed 6Mo austenitics were first applied, programs of comprehensive availability of all product forms through metal service centers, sponsored by Avesta Sheffield and by Allegheny Ludlum, have caused the 6Mo stainless steel to be accepted as a standard level of stainless steel performance. The lesson is clearly demonstrated that general commercial acceptance of a new stainless steel requires not only a significant technical/economic advantage, it also must have the commitment of the originating producer to continuing availability in the forms and quantities required by the end users.

The 6Mo grades have been used extensively in pulp mill bleaching systems, as shown in **Figure 3**, particularly those using chlorine or chlorine dioxide bleaching. For example, a washer vat constructed of 254 SMO has been in service since 1977 in an application where the 4.5 Mo, Alloy 904L perforated by pitting attack in six months. The 6Mo grades are well suited for handling tall oil, a by–product of some pulp production. The AL-6X condenser tubing has largely been superseded by AL-6XN tubing in utility condensers, with well over 13 million meters now in service, some of it for periods exceeding fifteen years (3). 6Mo service water piping in nuclear power plants using sea water for emergency safety systems have been in service since 1984. In another sea water handling application, shown in **Figure 4**, several thousand tons of 6Mo stainless steels have been used on offshore oil and gas platforms in ballast piping, fire control systems, and other applications characterized as critical or extremely expensive or difficult to maintain. In a more general way, the 6Mo grades, because they have been made available on a continuing basis by their sponsoring producers, have become maintenance materials to be used when 316L or other lesser alloyed stainless steel fails in service. The 6Mo grades have been used in food processing equipment, particularly where there is a potential for SCC and for extreme concentrations of chloride in preparation of certain foods such as processed meats and tomato-based sauces. Pharmaceutical applications where electropolished surfaces and absolute freedom from product contamination are essential, have made good use of these advanced, high performance stainless steels.

The addition of nitrogen enhances the strength and austenite stability in 4 to 5% Mo austenitic stainless steels. As a result, type 317LMN (UNS S31726) has become the standard material of construction for flue gas desulfurization scrubbers. As shown in **Figure 5**, these devices may require hundreds of tons of plate for a single unit. However, the reliability of performance of this high molybdenum austenitic stainless steel and its resistance to the operations upsets that occur in service make 317LMN the most effective materials selection on the basis of its life cycle costs.

The direction of future developments in austenitic stainless steels is clearly the further use of nitrogen for its own merits and for its ability to permit higher chromium and molybdenum additions. As discussed by Speidel, nitrogen additions as high as 1% are reasonably possible (6). Originally it was believed that it would be difficult to achieve more than about 0.25% nitrogen in regular production because higher nickel, typical of the more highly alloyed corrosion resistant materials, limits the solubility of nitrogen. However, it is now apparent that with correct balancing of chromium and manganese which increase nitrogen solubility, much higher levels are possible in conventional production equipment.

An example of the manganese approach is TEW 4565S (UNS S34565) which uses an addition of 6% Mn to increase the nitrogen solubility in a 24Cr-4.5Mo grade

5.

6a.

6b.

Figure 1. *Ferritic stainless steels such as 18Cr-2Mo (UNS S44400) provide excellent resistance to chloride stress corrosion cracking (SCC) in the conveyor chain for a hot dog cooking machine.*
Figure 2. *AL 29-4C (UNS S44735) provides efficiency and durability in the condensing heat exchanger for high efficiency, gas-fired residential furnaces.*
Figure 3. *The 6% molybdenum austenitic stainless steels have provided over 15 years of service in chlorine and chlorine dioxide pulp bleaching washers.*
Figure 4. *Several thousand tons of 254 SMO (UNS S31254) austenitic stainless steel have been used in ballast piping, fire control systems, and other critical systems where freedom from maintenance and reliability of performance are essential.*
Figure 5. *Type 317LMN, austenitic stainless steel with 4.25 Mo and 0.15 N, has become the standard material of construction for power utility flue gas desulfurization scrubbers because of its high reliability and low life-cycle costs.*
Figure 6. *High strength and resistance to pitting and chloride stress corrosion cracking SCC make 2205 duplex stainless steel (UNS S31803) a versatile and cost efficient engineering material. High strength permits reduced tank weight and increased payload in chemical tankers (a). SCC resistance makes 2205 a natural selection for brewery tanks and piping systems (b).*

to 0.5%. Unfortunately, this very high level of manganese is relatively aggressive to refractory liners of production equipment. Although this grade is stronger than the 6Mo-0.2N grades, it is only comparable in corrosion resistance. The relatively small cost savings in molybdenum may not offset the operational difficulties associated with high manganese. This is consistent with the observation that the manganese austenitic stainless steels developed during wartime to deal with nickel shortages have not replaced the nickel grades when nickel has been available, even with the nickel cost in some periods at more than ten times manganese cost.

A major advance in austenitic stainless steels is the Avesta Sheffield 654 SMO grade (UNS S32654) with 24Cr-22Ni-7.3Mo-0.5N. It is AOD refined and continuously cast, and is similar in processing and metallurgical stability to the 6Mo-0.2N grades (7). The 0.5N provides a significant increase in strength and the new combination of Cr, Mo, and N offers a chloride resistant stainless steel that approaches the resistance of Alloy C-276 (UNS N06276). The 654 SMO steel, first commercially produced in 1992, has been used in pulp mill bleach washers, flat plate heat exchangers for high temperature sea water, and chemical processing equipment where a nickel-base alloy would normally have been required.

A key factor in the evolution of the high performance austenitic stainless steels is the development of appropriate welding practices and corrosion resistant weld filler materials. The 6Mo austenitic stainless steels now have acceptable field experience in GTAW, SMAW, SAW, and PAW using nickel-base alloy filler metals with at least 9% Mo.

The key to further evolution of the austenitics will be the development of techniques of producing and controlling higher levels of nitrogen in the austenitic stainless steel, the identification of compositions with acceptable metallurgical stability for processing and fabrication, and the development of appropriate joining technology. Further evolution appears possible and merited.

DUPLEX STAINLESS STEEL

Duplex stainless steels can hardly be described as “new” when they were first produced over sixty years ago (8). However, it is possible to discuss first and second generations of duplex stainless steels based on the intentional and controlled use of nitrogen (9).

Nitrogen makes it possible to avoid two problems that regularly occurred when welding the first generation duplex grades. The first involves low heat input welds where a relatively small weld can be rapidly quenched by the workpiece itself. In this case a portion of the heat–affected zone (HAZ) will often become highly ferritic resulting in reduced toughness and lowered corrosion resistance. The second situation involves the total time (as distinct from heat input) of exposure at 700-1050°C in the HAZ. The first generation duplex stainless steels were susceptible to very rapid formation of intermetallic phases, such as sigma phase. Once formed, these intermetallic phases are exceedingly harmful to toughness and corrosion resistance and can be removed only by a full solution anneal and rapid quench.

Addition of nitrogen to the second generation of duplex stainless steels does not totally remove either of these problems. However, nitrogen does broaden the range of acceptable welding parameters sufficiently to permit practical fabrication and use of these highly versatile and cost effective grades. Even with high nitrogen it is still possible to get a highly ferritic HAZ, e.g., in small resistance welds; installation of thin-sheet liners on heavy plate or light-wall tubing seal welds on heavy tubesheets; tack welds; and subtle smoothing passes. Even with high nitrogen, the duplex grade can eventually form intermetallic phases due to repeated weld passes building cumulative exposure time. Unlike the special austenitic stainless steels where heat input in a given pass is a concern because of the risk of hot cracking the nickel-base filler, the duplex grades can tolerate extraordinary heat inputs without hot cracking, provided that total time at temperature does not exceed the time to precipitation of the intermetallic phases.

The second generation duplex grades have been used since the early 1980s and have provided outstanding service. The first and largest in terms of commercial development of these grades is the 2205 steel. The duplex stainless steels offer an unusually good combination of properties. The duplex grades are typically twice as strong as the common austenitic stainless steels. They allow the production of high chromium stainless steels, taking full economic advantage of the synergistic enhancement of the effect of molybdenum by higher chromium levels. The duplex stainless steels, although not immune to SCC, are highly resistant and so offer many of the advantages of the ferritic stainless steels without the difficulty of low toughness and welding limitations. While 2205 was the first and is commercially the largest of the duplex stainless steels, this concept has broadened into a family having a range of corrosion resistance nearly as wide as that of the austenitic family.

Welding technology for the duplex grades is different in significant aspects from the general experience of the austenitic grades and from that of the special austenitic grades, but in fact, with proper qualifications of procedures, is quite acceptable in terms of ease of welding and properties obtained.

The applications of duplex stainless grades have taken advantage of their strength, resistance to chloride stress corrosion cracking, and cost effective pitting resistance. The versatility of this class of stainless steels is demonstrated in **Figure 6**. The petroleum industry was a major factor in starting the market for second generation duplex grades through its requirements for a high strength stainless steel with good resistance to brine and carbon dioxide. One of the largest applications has been the use of 2205 in multi-cargo marine chemical tankers where 2205 offers corrosion resistance superior to the previously used 317LN and a lighter weight construction, and thereby, higher payload because of its high strength. In the paper industry, 2205 has been used in pulp batch digesters, bark handling systems, and applications where 316L and 317L have a significant risk of SCC. The 2205 duplex has been successful in a wide range of chemical and petrochemical processing equipment. While the duplexes are not immune to SCC, they provide a wider working range for the operators and a greater safety margin with respect to SCC than the common austenitic grades. Both 2304 and 2205 are candidates for food and beverage processing equipment where 304L and 316L would commonly be used, but they risk personnel safety and production interruption because of SCC.

The limiting factors in evolution of the duplex stainless steels appears to be similar to those of the austenitic grades, i.e., the need to introduce ever higher nitrogen to provide structural stability to the steel. In the duplex grades, dealing with half of the microstructure in the ferritic condition which is so sensitive to non-metallic and intermetallic phase precipitation makes this issue even more critical in terms of maintaining adequate properties in field applications.

FUTURE EVOLUTION

Stainless steel innovation continues. After more than twenty years, we are still far from recognizing and exhausting all of the possibilities provided by the AOD technology. Beyond that production approach, we have the practical possibility to achieve compositions impossible to cast uniformly through application of powder metallurgy techniques. Through the efforts of individual producers, the cooperation of industry associations, and the oversight of associations responsible for specifications and design criteria, the evolution of stainless steels in performance and economy continues today even as the industry contracts and reorganizes.

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THE INTERNATIONAL MOLYBDENUM ASSOCIATION (IMOA) was set up in 1989 and it has quickly earned its reputation as the focal point of reference for the molybdenum industry. There are member companies from every sector of the Western world's industry and China is also now represented. Although IMOA is registered under Belgian law, its secretariat is based in London.

The Association's activities centre around:

- the promotion of molybdenum as a competitively priced and abundant material, which gives to the products in which it is used maximum performance at minimum cost;
- molybdenum in relation to health, safety and the environment. With the increasing amount of legislation on metals, IMOA provides a central service which saves individual companies time and money;
- the collection of statistics on the molybdenum market. Production, consumption and inventory data is collected and summarised both regularly and confidentially;
- the organisation of regular meetings and conferences at which the industry can meet to exchange views, make new business contacts and learn about the latest technical innovations;
- preparation of guidelines on sampling and assaying procedures.

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