

# INTERNATIONAL MOLYBDENUM ASSOCIATION

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Would readers note our change of address and phone and fax numbers. Our e-mail and website addresses remain the same.

Michael Maby, Secretary-General of IMOA, apologises for not publishing the January issue. Some readers even noticed! Pressure of work occasioned by the departure, after 7 years' service, of my secretary and a decision to find a new office meant that I had to miss the first issue in 11 years. IMOA (and ITIA) is now happily re-located and Kumi Patel has sacrificed an easy life to work for me.

# 12th Annual General Meeting

# 15-17 November Hotel Royal Monceau, Paris

The meeting has been scheduled to precede Metal Bulletin's Ferroalloys Conference, 19-21 November, in Paris but at a different hotel.

Details of the programme have still to be finalised, but an outline follows:

# Wednesday, 15 November:

14.00 - 17.00 Meeting of the HSE Committee

# Thursday, 16 November:

14.00 - 17.00 Meeting of the Executive Committee

# Friday, 17 November:

10.50 - 10.00 AGM	10.30 -	16.00	AGM
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19.00 - 22.30 Cocktails and dinner in the hotel

# **Presentations will include:**

- An update on IMOA's activities in relation to the Market Development Programme
- A report by H Pariser on the Market Survey
- Reports on work of the HSE and Sampling & Assaying
   Committees
- A paper by a guest speaker on a general topic, perhaps e-commerce

Companies which are not members of IMOA should contact the Secretariat for information about participation.

# This Newsletter contains articles of interest, including:

- IMOA's activities regarding market development
- Moly does the job in nuclear power applications
- Summaries of four papers at recent Stainless Steel Conferences which dealt with successful applications of duplex in various industries.

# Membership

It is a pleasure to announce the membership of :

Teledyne Advanced Materials, a powder and alloy stock supplier; and

Liaoning Chaoyang Dongfeng Ferroalloy Plant, a producer of tech oxide and FeMo.

On the other hand, the resignation of the following companies is mentioned with regret: Montana Resources North Metal & Chemical Co Sekom Handelsges. MbH

# Moly does the Job

# Summary

A North American nuclear power plant originally had a lined carbon steel service water piping system. The system began to deteriorate within a few years of installation, especially at the welded joints of the carbon steel piping. In a first repair phase, the lined carbon steel piping was relined or replaced with Type 304 and Type 316 stainless steel. However, neither the relining nor the lower alloy stainless steels performed adequately. In 1986, small quantities of 6% molybdenum stainless steel piping began to be installed. On the basis of initial troublefree performance, many thousands of feet of this piping have since been installed. Inspection cycles can now be extended to twice the normal time, and could potentially even be extended to three to four times the normal time, because of the great performance of this highly corrosion resistant stainless steel. The plant is now saving over \$1,200,000 in maintenance and inspection costs and over 1200 staff-hours every cycle of eighteen months.

# **The Process**

A service water system at a nuclear power plant is a piping system that carries cooling water to various heat exchangers. It removes the heat from such auxiliary systems as component cooling heat exchangers, emergency diesel generators, containment coolers, lube oil coolers, room coolers and chiller condensers.

Typically, a system consists of an intake system for the cooling water, a distribution system within the plant and an outlet structure.

In this case the service water system is open loop and is fed by high chloride brackish water which can range in temperature from 32°F (0°C) to 85°F (29°C). Part of the service water system is above ground and some is buried.

Most of the original service water system was constructed of lined carbon steel pipe. Various linings were used including coal tar epoxy, epoxy enamel and cement lining for the larger diameter pipe sizes, cement lining for smaller diameter sizes, and some polyethylene lining. Minor portions of the original piping were Type 316 stainless steel.

# The Corrosion

Extensive weld metal and heat affected zone corrosion was observed on the carbon steel piping where the cement lining had cracked at the welds. Polyethylene linings failed due to erosion, which lead to subsequent erosion and corrosion of the underlying carbon steel base material. The Type 316 stainless steel failed due to through-wall pitting corrosion in areas of stagnant water within three years of operation. Galvanic corrosion was observed in joints where carbon steel and stainless steel were welded together. Mating surfaces of Type 316 stainless steel and of rubber lined carbon steel valves showed pitting and crevice corrosion. Finally, extensive exterior corrosion was observed on carbon steel piping under insulation where condensation water was kept in contact with the (unlined) carbon steel.

The brackish, silt-containing water caused the corrosion and erosion on the lined carbon steel in places where the lining was flawed or eroded. Carbon steel has no inherent corrosion resistance under these conditions if the lining fails for any reason.

Type 316 stainless steel is usually resistant to water containing up to 1000-ppm chlorides as long as a sufficient flow rate (approximately > 3-ft. (1m)/ sec.) is maintained. The chloride content of the brackish water at this site varies from 85 to 7,200-ppm, and the flow rate is as low as 0 for extended periods of time in the areas where Type 316 piping was installed. These severe conditions lead to the relatively rapid pitting corrosion failure in some of the stainless steel piping.

# The Solution

About ten years into the operation of the power plant, it became apparent that the replacement of some of the lined carbon steel with Types 304 and 316 stainless steel was not a permanent solution. In 1986 the power plant started to install small amounts of highly corrosion resistant 6% molybdenum containing stainless steel. More of the high performance stainless steel was installed at every refuelling outage and thus all of the above ground service water system was gradually replaced. Today only a few spool pieces of lined carbon steel remain in the system. *Figure 1* shows one of these remaining pieces that is exhibiting extensive corrosion. These pieces are very difficult to replace because they penetrate concrete walls and are anchored to these walls. Nevertheless, the engineering staff is in the process of finding ways to replace these last pieces of carbon steel in the system.

The majority of the Type 316 valves and the rubber lined carbon steel valves have also been replaced with 6% molybdenum stainless steel or with aluminum bronze.

The plant has been extremely pleased with the performance of the 6% molybdenum stainless steel. The piping hardly requires any maintenance and no longer needs to be inspected during each outage. All of it remains in perfect condition. *Figure 2* shows the interior of the pump discharge distribution header made of 6% molybdenum stainless steel. The stainless steel has been in continuous service for 30 months and had not been cleaned before this picture was taken. The total time in service for this part of the piping has been six years.

# The Cost Savings

In the early eighties, before the 6% molybdenum stainless steel replacement, maintenance and repair of the lined carbon steel service water system were about 40% of the annual maintenance budget of the plant. In those days the pitting corrosion had to be ground out and repair welded wherever the pipe wall had thinned excessively, and then extensive relining was required. These repair expenses are no longer incurred with the new system.

Other cost savings are related to inspection and maintenance of the system. The old system had to be inspected during each refuelling outage, which is about every eighteen months. This inspection alone cost the power plant \$1,200,000 and 1200 staff-hours without any repair being performed. Today the 6% molybdenum stainless steel system allows the plant to skip every other cycle and perform the inspection only every 36 months. Because the piping remained in perfect condition after over thirty month of operation, it is estimated that the maintenance cycle can be extended even further, to every third or fourth outage. In addition to the direct cost of materials, contractors and inhouse labour, the repair of the lined steel service water system also took much time. One day of lost electricity production can cost a nuclear power plant several hundred thousand dollars. To become more cost competitive, nuclear power plants have to continually reduce their outage times. This became only possible for this plant because the new 6% molybdenum stainless steel piping does not require any repair.

# "Once again - Moly does the Job."

 Table 1: Typical Chemical Compositions of the Stainless Steel Grades in this Article. Note: 254 SMO, AL-6XN, INCO alloy

 25-6MO and Cronifer 1925 hMo are all 6% molybdenum stainless steels.

	UNS No.	Molybdenum	Chromium	Nickel	Nitrogen	Other
Type 304	S30400	-	18	9	-	
Туре 316	S31600	2	17	11	-	
254 SMO*	S31254	6	20	18	0.2	0.75 Cu
AL-6XN®	N08367	6	20	24	0.2	
INCO <sup>®</sup> alloy 25–6MO	N08926	6	20	24	0.2	0.75 Cu
Cronifer <sup>®</sup> 1925 hMo	N08926	6	20	24	0.2	0.75 Cu

The 6% molybdenum stainless steel names are protected trademarks of the following companies:

254 SMO	Avesta Sheffield	AL-6XN	Allegheny Ludlum
INCO alloy 25-6MO	Special Metals	Cronifer 1925 hMo	Krupp VDM

Figure 1: Lined carbon steel spool piece from intake structure. Significant corrosion can be observed on the edges of the pipe, where the lining has imperfections.





Figure 2: Interior of the pump discharge distribution header made of 6% molybdenum stainless steel before cleaning. After 30 months of operation no corrosion or other build up has formed on the pipe walls.

# **IMOA's Duplex Project**

Entering its third year, this project has excited the Stainless Steel industry as evidenced by messages of congratulations on the technical content of the brochure "Practical Guidelines for the Fabrication of Duplex Stainless Steels" written for IMOA by Technical Marketing Resources and published last year. The brochure was supplemented by IMOA training seminars on the fabrication and welding of duplex (reviewed in the July 1999 Newsletter). Several of these seminars have since taken place in the USA and Europe and clients have included Phoenix, Freeport Welding, FMC, Curtis Kelly, Clausthal-Zellerfeld Technical University, Dupont Chemicals, The Steel Plate Fabricators Association and Hicks Equipment (and some of these companies brought along delegates from their own customers). Further seminars are planned in Europe in conjunction with the Stainless Steel Development Associations in Germany, Italy and the UK and interest has been expressed in a co-operative programme by the Stainless Steel Development Associations of Australia and Brazil.

Time will tell about the effect on duplex usage in tonnage terms (and moly consumption), but if IMOA had done nothing to promote duplex and help educate engineers to overcome technical problems, and to encourage those responsible for alloy selection by the provision of information, it is certain that progress would have been slower.

Act or do nothing...IMOA is in no doubt about the choice and will continue vigorously to promote moly, based on expert technical advice, and consult with all sectors of the industry, including not only consumers and end-users of products but also IMOA's counterparts, NiDI and ICDA.

Now read on regarding IMOA's ambitious plans for the future...

# **MARKET DEVELOPMENT PROGRAMME**

The Association is in the process of exploring the main potential areas for increasing moly consumption. As these areas are identified, the programme will be expanded to develop ways and means to promote moly usage therein. A summary of the programme's main points follows:

- The success of the duplex project, by providing consumers with technical information on fabrication and welding, is evidence that IMOA should focus on other end-uses and supply similar expertise
- A market survey will be conducted by the consulting firm, Heinz Pariser in Germany, to identify new opportunities for moly consumption. Past and current trends will be analysed and the main potential areas to develop consumption will be suggested
- How best to take advantage of the potential will be examined and a programme implemented, which will include the employment of a full-time IMOA technical officer

The commitment to this ambitious and exciting programme by the major producers and converters of moly provides a focus to the Association's activities for several years to come. The commitment is also to consumers of moly, by providing technical expertise about its unique properties and usage, and a continual flow of information about moly in relation to health, safety and the environment.

# IMOA's Involvement in Stainless Steel / Duplex Conferences

As part of IMOA's thrust to promote and explain the technical and environmental benefits of using moly in the Stainless Steel industry, the Association has sponsored, and participated in (papers, session chairpersons), two recent conferences. A further aim was to expose and publicise the name of IMOA and its activities to worldwide audience and no company using moly can now claim never to have heard of the Association.

Heike Helfen (Climax Molybdenum GmbH) attended both conferences and wrote this report for IMOA, summarising the conclusions of four papers which deal with successful applications of duplex in various industries.

# "Stainless Steel World 1999"

# 16-18 November 1999, The Hague, The Netherlands (organised by Stainless Steel World)

(1) Some duplex applications – Test results and practical experience Authors:

Jacques Charles, Michel Verneau, Jean-Pierre Audouard and Sophie Demars (Creusot-Loire Industrie – FAFER)

In recent years, the use of duplex stainless steel has grown dramatically, particularly in the oil and gas, pulp and paper and chemical industries as well as for chemical tankers. However, the high strength of this material makes it also suitable for numerous other applications.

# **Pulp and Paper:**

In the pulp and paper industry, duplex stainless steels have been used for at least 30 years. Applications include chip preparation, chemical pulping, bleaching, paper machines, recovery and steam plant equipment. The emergence of duplex applications in this area results from their superior mechanical strength, wear and cavitation resistance, fatigue strength, stress corrosion cracking resistance and corrosion resistance.

# **Chemical and Petrochemical:**

In the chemical and petrochemical industries, high temperatures and the presence of chlorides at high or intermediate concentrations characterise the corrosive environments. In combination with applied stresses, these media generally induce stress corrosion cracking. So far, applications for duplex or superduplex in these areas have been PVC stripper columns and heat exchangers, pressure vessels for organic products or reactors for the oxo-alcohol production.

# **Phosphoric Acid Plant:**

Other examples for the successful use of, notably, superduplex stainless steels are phosphoric acid plants, including agitators. More than 95% of phosphoric acid is produced using wet processes, where natural phosphate rocks are attacked by sulphuric acid. The corrosion is enhanced by temperature, impurities (fluorides, chlorides) and erosion corrosion phenomena. The slurry contains up to 40% particles in suspension, mainly gypsum and silica. As a consequence, parts of the equipment (mainly agitators and pumps) are submitted to very severe erosion corrosion processes. And in the past some pumps or agitators had to be replaced each year!

# Flue gas desulphurisation:

In 1986, the industrial application of superduplex for scrubbers in flue gas desulphurisation units started. The most common technology consists of scrubbing the SO2 containing gas with slurry of lime or limestone in water. In certain areas of the scrubber, where the reaction between polluted gas and the solution is not complete, acidic condensation may occur and, combined with temperature, chlorides and/or fluorides lead to very aggressive conditions. Since 1986, other installations and equipment, including internal structure and lining in the FGD units (e.g. centrifugal fans, absorbers, expansion joints and dampers and heat exchangers), have been realised using duplex or superduplex stainless steels.

# Cargo tanks for chemical tankers:

In order to avoid contamination of the cargo as well as damage to the tank itself the steel used for cargo tanks for marine chemical tankers has to be resistant to different corrosion mechanisms. In the past, austenitic stainless steels were selected for most marine cargo tanks. Now, duplex stainless steels are more and more specified.

# **Onshore / Offshore:**

In the onshore/offshore area, duplex and superduplex stainless steels have been used successfully for vessels, separators, risers, flow-lines, process pipes and seawater systems. The high corrosion resistance, including sour gas conditions, as well as the high mechanical properties, explain this popularity in the on/offshore business.

# Art and Architecture:

Due to its high strength and corrosion resistance, duplex stainless steel has been successfully used in several architectural applications. One example is the Grande Arche in Paris La Défense.

#### (2) Welding of stainless cargo tanks for chemical carriers Author: Jörgen Strömberg, ESAB AB, Sweden

Today, the majority of chemical tankers are constructed to be able to carry a variety of chemicals, even different ones at the same time in separate tanks. The implication for hazardous or toxic material and more aggressive chemicals in the future is a major issue to be considered during design, construction and, especially, material selection. Some of the main criteria for selecting the correct steel grade are:

Corrosion resistance (against various chemical media to be shipped)

- Life cycle
- Maintenance
- Material cost
- Mechanical strength
- Weldability
- · Fabrication costs (forming, cutting, welding)
- Cleanability (to avoid contamination)

The types of corrosion that can be found in marine chemical tankers are general corrosion, pitting and crevice corrosion. The most serious corrosion damage is normally associated with phosphoric acid, sulphuric acid or cargoes containing halogen ions as chlorides. One particular problem can be the dilution of seawater when cleaning the tanks in order to avoid any contamination of the different cargoes.

Due to its good corrosion resistance against a variety of different chemicals duplex stainless steel (2205) has been used to manufacture almost all cargo tanks for new chemical tankers within the last decade. As the cargo tanks directly contribute to the strength of the hull structure, another benefit is derived from the excellent mechanical properties of duplex stainless steel. Because of its high strength the plate thickness could be reduced, leading to a reduction of the payload. Using duplex instead of austenitic stainless steel can reduce the weight of a tank by 10-15%.

Welding is an essential part not only of fabricating the tanks but also of building the whole vessel. Modern nitrogen containing duplex stainless steels have a very good metallurgical weldability. The addition of nitrogen sufficiently broadens the range of acceptable welding parameters to permit practical fabrication. Duplex weld metals are not sensitive to hot cracking and, due to their lower thermal expansion, duplex steels show less deformation than austenitic steels during welding. Experience has shown that following established welding procedures causes few problems. However, the training of welders and foremen is very important, especially before launching new projects.

# "Duplex America 2000"

# 29 February – 1 March 2000, Houston, Texas (organised by Stainless Steel World)

(1) Life cycle cost evaluation of carbon steels, austenitic and duplex stainless steels for storage tanks Authors: Jean-Pierre Audouard, CLI-FAFER, France Christophe Dernoncourt, CLI-FAFER, France

For the last decades, carbon steel has been used extensively to build storage tanks, especially for the petrochemical industry, food industry, water treatment units and parachemical industry. Although painting and coating have to be applied to protect this material against corrosion, even in the atmosphere, the use of coated carbon steel remains routine practice due to its availability, low cost and ease of fabrication.

However, detailed analysis of capital investment costs, as well as life cycle costs, is available to demonstrate clearly that stainless steels are cost-competitive. Especially duplex grades due to their higher mechanical strength appear to be less expensive than coated carbon steel although not all national pressure vessel codes permit full advantage to be taken of these properties.

The selection of a high strength material like duplex stainless steel allows a reduction of the wall thickness. The related cost savings are significant, not only for the material and for forming costs, but also for welding operation costs (less weld material, reduced welding time). In addition, the weight reduction decreases several indirect costs such as transportation or erection costs.

Furthermore, due to their higher corrosion resistance, stainless steels do not need to be painted or coated. With respect to a lack of corrosion resistance in many environments, the necessary coating and painting of carbon steel imply heavy additional costs, especially when labour costs are important. Moreover, coatings often need regular maintenance operations, which lead to a further increase of cost. Based on their evaluations the authors were able to summarise the different cost-factors for comparison (Table 1).

#### Table 1: Sum-up of the main costs for four different materials (Remarks: \*2304, \*\*2205)

Costs in 1.000 US\$	A 516 gr. 60	316L (austenitic)	UR 35N*	UR 45N**
	(carbon steel)	(2.5%Mo)	(duplex)	(duplex)
Material	79	290	241	321
Forming	29	34	35	35
Welding	241	252	243	240
Pickling	0	45	57	57
Coating & Painting	333	0	0	0
Total Investment	682	620	576	653
Maintenance	450	0	0	0
Total Life cycle	1132	620	576	653

During recent years, numerous storage tanks made of duplex stainless steel were used to replace carbon steel tanks in the pulp and paper as well as in the chemical industry. In general, the cost analysis conducted by end users confirmed the cost benefits induced by using duplex. It turned out, that after 2-3 years in service, the duplex tanks proved to be much cheaper than carbon steel tanks because maintenance operations could be avoided completely.

(2) Increased usage of duplex materials in manufacturing of pulping equipment *Authors:* 

Alpo Tuomi, Valmet Engineering Pulping Oy, Finland Allän Löfstrand, Valmet Engineering Pty Ltd., S.Africa Mikko Harju, Santasalo Engineering Oy, Pori Finland

In many industrial areas, e.g. the pulp and paper industry, the chemical processes are intensified and tightened.

Consequently, materials that are more corrosion resistant have to be used to manufacture the pulping equipment.

Today, almost all pressure vessels used in the pulp and paper industry are made of duplex stainless steels. These vessels include mainly digesters used for the cooking of chips in alkali conditions, as well as reactors in the oxygen delignification and bleaching processes, which work in both alkali and acid process conditions.

The main reason for the increased usage of duplex in the pulp and paper industry is obviously the economic benefit resulting from material savings due to the favourable strength properties of this material. The following table shows the relative prices of different materials used for the fabrication of pulping equipment.

Material	% <b>Mo</b>	Price Factor (European)
304L	-	1
316L	2.5	1.3
2304	-	1.5
2205	3	1.6
317L	3	2.3
2507	4	3.0
904L	4.5	3.4
254 SMO	6 4.7	654
SMO	7	7.5

It is interesting to note that, compared to 904L, the 2205 duplex material shows a very good "pitting resistance against price" value. Although both materials have the same pitting resistance equivalent (PRE), the price of 904L is twice as high. However, as impurities, acid concentrations and other issues can have enormous effects on the corrosion resistance of a material, this comparison should be used with caution.

A typical pulping process consists of various process steps: pulp digesting, washing and screening, oxygen delignification and bleaching. Moreover, the prediction is that duplex materials will be able eventually to replace most austenitic materials in the pulp and paper industry with a few exceptions in the bleaching process. In particular, the molybdenum containing 2205 duplex grade is gaining more and more popularity within the pulp and paper community, not only because of its high strength and excellent corrosion and erosion properties, but also on a cost basis. Hence, it is now used not only for pressurised vessels (e.g. batch digesters or reactors), but also for filter drums, pulp conveyor screws, wash presses, storage tanks and some bleach filters.

IMOA will also be sponsoring the 6th World Conference "Duplex 2000" organised by the Associazione Italiana di Metallurgia in Venice from 17-20 October and already a total of 113 papers from fabricators, researchers, end-users, engineering and service companies from 29 countries, have been selected.

AIM has commented that past conferences focused on fundamental aspects: structural stability, weldability, resistance to corrosion, specific applications and costbenefit analysis. Recently, the production and use of duplex stainless steel has grown as a result of the development of technologies which have enabled an increase in quality and reduction in fabrication and transformation costs. The peculiar characteristics of these materials already make duplex stainless steel a strategic choice in many applications. It is now time for a global analysis of duplex stainless steel metallurgy in order to obtain an overview of the achievements of research in fabrication, development of new products, their characterisation and utilisation.

# Other forthcoming conferences to be noted are:

Stainless Steel World Conference and Expo on corrosion resistant alloys 13-15 November 2001 in The Hague

British Stainless Steel Association Conference and Exhibition 9 November 2000, Birmingham

## **Designing and Building with Stainless Steel**

20 November 2000, Milan - organised by Centro Inox in collaboration with Euro Inox

#### **Correction:**

In the July 1999 edition, in an article entitled "Investigation of Corrosion Resistance of Duplex and 4-6% Mo-containing Stainless Steels in FGD-Scrubber Absorber Slurry Environments" an error occurred in paragraph 3, second sentence, regarding the temperature. The sentence should have read "The slurry pH was typically around 5.5 and the temperature in the 120° to  $154^{\circ}F$  (~  $49^{\circ} - 68^{\circ}C$ ) range". Apologies to all, especially to NiDI which initiated the project and to LaQue Corrosion Services which wrote the report from which abstracts were quoted.

# тм

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