Past, present and future of weldable supermartensitic alloys

Authors:
H. van der Winden, Fairwind Materials Consultancy
Patrick Toussaint, Industeel Belgium (Arcelor Group)
Lionel Coudreuse, C.R.M.C., France (Arcelor Group)

Keywords:
Supermartensitic, alloy development, weldability, stress corrosion cracking, hydrogen

1 Abstract
Weldable supermartensitic alloys have been introduced to the oil & gas industry some 5 years ago and have shown considerable development on various aspects. The paper will address the main achievements as well as some issues that require further development work. Special attention will be given to some problems that have occurred recently.

2 Introduction
Since the mid 90’s, weldable supermartensitic alloys became available and have been applied in increasing quantities, almost exclusively in the oil & gas industry so far. Many operators had already extensive and very positive experience with the non-weldable grades (notably AISI 410), mainly for downhole applications. Between the early weldable grades that were offered and the grades that are now on the market, significant differences have developed. This paper will pay attention to some of those historical developments but will mainly focus on the topics that may currently give concern for further application of the weldable supermartensitic alloys.

3 History
The first large scale application of 13% Cr steel for a pipeline/piping system was Mobil’s Arun field where from 1980 onwards centricast pipe material (AISI 410) was used. In order to obtain sufficient toughness, even for the fairly benign ambient conditions in Indonesia, very extensive preheating and post weld heat treatments had to be used. The installations are still operating successfully. Nowadays such a grade would not be considered very weldable as most current applications have toughness requirements that could never be met by the classic 13 Cr alloys.

The introduction of genuinely weldable grades started around 1995 when both Statoil and NAM started to pre-qualify seamless pipe materials for flowline projects. Statoil, for their offshore Åsgard and Gullfaks projects 1), selected medium and high grade material because of the presence of some H₂S, while NAM opted for the lean grade for their sweet service, onshore flowlines.

Shortly thereafter NAM started the pre-qualification work for large diameter SAW pipe for an onshore fingertype slugcatcher 2). This material was ordered and supplied but before construction and installation were executed, the expansion activities for the Anjum treating plant were aborted as a result of national politics reasons. Nevertheless, the order was considered a technical success. In parallel, the development and qualification of seamless and welded fittings for piping and pipeline systems was also completed successfully, including all necessary welding qualifications.

In the late 90’s the development of thin-walled, seam welded pipe was taken up, firstly by Japanese suppliers. This development aimed to use the existing high-speed pipe production lines also for SMSS materials. Due to various technical problems and to a fundamental re-structuring of the Japanese steel industry, the introduction of this pipe material on a larger scale has suffered a (temporary) set-back.

4 Achievements
In the still fairly limited period since the start of the development of weldable supermartensitic materials, quite a lot has been achieved. It should be realised that this has been done by the industry
as a whole, so not only by the developers/suppliers, but also by operators, scholars, consultants and authorities. All have played, and are still playing, their role. From the very many achievements made, only the major ones are discussed below.

4.1 Stable alloys
The Fe-Cr-Ni phase diagram, in the compositional range of interest, is pretty complex through the various phase transformations during heating and cooling. Also, the cooling rates lead to the presence of various meta-stable microstructural elements that may transform during later manufacturing steps or during the period when the materials are in actual service. In fact, the art of designing a supermartensitic alloy is a metallurgical balancing act just inside the martensite area but almost at the border where ferrite and/or austenite can be formed 4). The main reasons for this are to obtain good mechanical properties while limiting the alloying cost by using the range of ferrite and austenite formers available. At the same time the desired corrosion properties must be obtained by effectively using a careful mix of the appropriate alloying elements for this purpose. Other fundamental requirements are to reduce carbon and nitrogen for improved weldability and ensure extremely clean steels for getting the good toughness properties. And last but not least, these QT-steels must be given the correct heat treatment, particularly the tempering treatment is important. A very practical aspect is that the supermartensitic alloys easily tolerate successive heat treatments without losing out on their original mechanical properties.

Although there are still a few open ends, there is now a sound and fairly complete understanding on how the supermartensitic alloys behave in a metallurgical sense, under the various treatments that they may be subjected to. Each major steel supplier is now capable of giving the appropriate support to e.g. pipe manufacturers on how to treat their materials in order to obtain the optimal properties for the application in hand. In order to cover the potential application range of the oil & gas industry, three grades have gradually emerged: lean, medium and high alloyed SMSS 5)). Within such a grade each manufacturer may offer their optimal choice for the specific application. It should be noted that the grade indication is currently used as a coarse identification means only; a lot of work still has to be done before this can develop into standard grades with their guaranteed and internationally recognized properties.

4.2 Proven weldability
The initial welding trials were performed using the manual GTAW process with DSS consumables. Soon it became clear that good welders with experience in duplex stainless steels had no problems with welding SMSS alloys. The low production rate of the GTAW process however asked for trials with faster welding processes and procedures. So, manual and mechanized GMAW procedures, still using DSS or SDSS consumables, were developed 6). These efforts confirmed the excellent weldability of the supermartensitic alloys: skilled welders could easily obtain a fine appearance of the weld and avoid weld defects. Moreover, the mechanical properties of the weldment could meet essentially the same requirements as were set for the base material. For the fabrication of thick-walled pipe, SAW procedures were developed using DSS and SDSS consumable materials 7). In general, also with this process, the good weldability of the supermartensitic alloys was shown. The use of DSS/SDSS consumables was not considered optimal, mainly because of costs, the possible complications with undermatching weld metal yield and the inability to perform heat treatments after welding.

Therefore the use of consumables with an essentially matching chemical composition was taken up. Very promising results have been obtained so far but as can be seen in chapter 5.4 of this paper the development phase is not yet over completely. All pipe girth welding processes were so far aiming at avoiding post-weld heat treatments if at all possible, because PWHT represents a substantial cost-increase for pipeline welding, particularly for offshore pipelines. Generally, good weldability without PWHT can be achieved whilst maintaining acceptable, fit-for-purpose mechanical properties. In the light of the possible occurrence of SCC in the HAZ however it is unclear as yet whether this PWHT-free approach can be maintained for all applications.

When welding martensitic materials, hydrogen is a wellknown threat. Hence, all welding activities have paid due attention to avoid hydrogen pick-up by using low-hydrogen type welding processes, consumables and welding procedures. Essentially the same hydrogen precautions were used as is customary for duplex stainless steel. By doing so, cold-cracking could generally be prevented. However, in a rather special case, hydrogen did contribute to a pre-service failure in a reeled, so cold deformed, pipeline for StatOil 8). A thorough investigation revealed that the hydrogen level of the duplex filler material was too high for the particular situation: annealing of the welding wire solved the problem. Further consideration to this issue is given in chapter 5.5 ‘Hydrogen and supermartensitic stainless steels’.

Another issue of initial concern was excessive oxidation at the inner bore of pipeline girth welds. As SMSS alloys rely on a passive layer for corrosion protection, it is clear that irregular oxidation layers would have a negative influence on the corrosion resistance of the weld. Therefore it was generally
accepted that the level of protection of the inner bore should be equivalent to that used for duplex welding. This has proven to be effective, although for sour service more stringent requirements may be necessary.

4.3 Pipeline construction
So far, more than 600 km of supermartensitic pipelines have been constructed all over the world, so there is now a considerable amount of experience at operators and their contractors. The first offshore projects used the bundle approach, constructed onshore and towed out to their offshore location. Also the reeling method was developed and used for a 16” pipeline for Statoil. Recently an offshore project in Vietnam, employed S-lay welding of a 4.5 km 16” in-field flowline was successfully completed.

Onshore projects were completed at several places, e.g. in The Netherlands, in Nigeria and in Oman. Although every project may encounter its specific difficulties, it can be stated that several international contractors have now obtained a good level of experience with the construction and installation of supermartensitic pipelines.

4.4 Major corrosion processes

4.4.1 Sweet corrosion
During the pre-qualification work for the various SMSS pipeline projects it was confirmed that the behaviour of the new alloys in sweet CO2-containing media is very similar to the classic 13 Cr alloys. The material shows rapid repassivation once exposed to the corrosive medium. Also welding did not have much influence, in spite of the presence of some oxidation of the weld area. As a precaution however, excessive weld area oxidation is prevented by applying good back-shielding. When coupled to DSS/SDSS weld metal or -components no significant galvanic effect has been found. For higher temperatures, say about 150°C and up it is recommended to select the Mo containing grades as they show a superior resistance towards localised corrosion.

In the current absence of a solid set of corrosion data, all individual alloys had to be verified extensively against the anticipated worst conditions of the specific project.

It should be emphasized that, other than duplex stainless steels, in wet, sweet oil & gas conditions, these materials show a very limited general corrosion rate rather than no corrosion at all. This should be taken into account during the materials selection and the mechanical design process.

4.4.2 Seawater corrosion
In accidentally flooded pipelines it has been found that, within a few months, bioactivity can develop that can lead to localised corrosion with the potential to generate hydrogen underneath the biofilm. The investigation in such a case led to the requirement that the exposure time to uninhibited seawater should never be longer than one month.

External exposure to seawater is prevented by adequate coating systems that are backed-up by cathodic protection. For the latter subject read also chapter 5.2.2.

4.5 General
The above list of achievements is not necessarily complete: many more problems have been solved than can be included in this paper. Nor do the list imply that with the above aspects no problem can ever occur. Supermartensitic alloys do rank amongst the sophisticated alloys for which trouble-free application requires a high level of know-how and experience.

5 Main topics for development

5.1 Intergranular stress corrosion cracking at elevated temperatures
The intergranular stress corrosion cracking at elevated temperature as has been found pre-dominantly during qualification testing of some girth welds, appears to be very complicated due to the many parameters that may play a role. Several laboratories and institutes have initiated research programmes to unravel the problem. In addition, a concerted industry effort is underway to monitor and support these activities. In the so-called ‘SCC Forum’ experts from all corners of the materials world discuss results and try to develop jointly a model for the cracking mechanism.

The exchange of views intends to improve the understanding of the many pieces of the jigsaw puzzle and may lead to adjustment of experimental programmes. Key players on the experimental side are currently Sintef (supported by Statoil and BP) and CRMC (Industeel France), and the many pieces of the jigsaw puzzle may be a part of the many pieces of the jigsaw puzzle.

Although it is still early days, the contours of some possible clues are becoming a bit visible now from the early, sometimes tentative findings below:

- Cracking was only found in girth weld HAZ’s that had seen another ‘heat treatment’ from the subsequent weld pass. SAW seam welds did never crack.
- SMSS can develop sensitised area’s with precipitation of Cr-carbides surrounded by a Cr-depleted zone, albeit a rather small one.
- The surface condition of the steel, notably excessive oxidation, plays an important role in
initiating the cracking. Specimens with a machined surface could not be made to crack.

- A machined surface notch in a sensitised microstructure does not lead to intergranular cracking.
- The initial assumption that hydrogen contributed to the cracking process has proven rather, if not very, unlikely because the cracking could be reproduced in H2S free media as well.
- A short PWHT, typical 5 min. at 650º C, eliminates sensitisation and cracking.

It should be emphasized that the above findings are still in different stages of consolidation. Much more work to confirm these statements for a wider range of materials and conditions is absolutely necessary.

Important open ends still are:

- The roles and importance of initiation- respectively propagation mechanisms.
- The crack initiation conditions/mechanism
- Testing methods/procedures (e.g. the 4-p bend test with unmachined specimens) are not well defined and may lead to scatter which frustrates the analysis; this needs to be reviewed and aligned between laboratories.

Possible long-term solutions could include:

- Adjustment of alloy composition (stabilisation or suppressing/avoiding precipitation)
- Avoiding surface conditions that promote crack initiation
- Adjusting the welding procedure (preheat, interpass temperature levels, PWHT)

Although the current members of the SCC Forum do the best they can, within the limits of their ability and availability, the progress so far has been less than desired. More industry data from outside the Forum span of control would be very welcome. Only through a really joint industry effort one may expect that this industry-wide problem can be solved in a relatively short time.

5.2 Hydrogen and supermartensitic stainless steels

5.2.1 Pre-service

The current stringent precautions for preventing hydrogen entering the steel during welding have generally shown to be successful, i.e. cold cracking is being prevented. It must be realised however that the approach is still rather empirical, not the least because accurate modelling in a complex weld configuration is rather difficult. Also, the amount of experience data is still rather limited so one cannot always feel comfortable with a certain welding procedure because others have done it successfully before. So, the combination of a high strength material, the presence of various different microstructures around the weld and not very wellknown stress/strain distributions in the weld area may call for a more fundamental approach which may include component testing in addition to the now customary small sample testing.

5.2.2 In-service

The most common sources of hydrogen are:

1. from sour service conditions, leading potentially to sulphide stress cracking (SSC)
2. generation at local acid and low potential conditions in active pits or crevices
3. generation at conventional cathodic protection by sacrificial anodes

It is no surprise that the very strong and hard supermartensitic alloys have a rather limited resistance to sour service conditions. It is in fact impossible to satisfy for instance the NACE hardness maximum of HV 250. Although generic data are not yet available, the extensive project based test programmes have given a clear indication what these alloys can withstand and what not.

The work on SSC has been, and is being executed largely on a project-by-project basis in order to establish safe limits for the alloys under investigation. Because of the many variations between projects and the still limited amount of data, more generic resistance data are not yet available. In many cases the EFC-17 document has been followed but even then significant deviations are possible which makes a direct comparison of test results very difficult. A more stringent description of the test methodology appears to be necessary.

Localised corrosion during service can result from deposits accumulating in a pipeline and/or from the presence of oxide scales at the inner bore of the girth welds. During the welding precautions are being taken to reduce oxidation of the weld area but the level of control over the end result is not always satisfactory. A more reliable method could be to execute a cleaning pickling and passivation operation before the pipeline is taken into service.

Although pipelines are (initially) well protected by suitable coatings they inevitably will be exposed to seawater locally. The traditional second line of defence is a cathodic protection system, for longer pipelines usually by means of sacrificial anodes. On the high
strength SMSS materials such systems may do more harm than good because the inevitable degree of overprotection can lead to the generation of too much hydrogen. In a recent case this has led to the development of leaks around anode attachments. It should be stressed however that this mishap is by no means unique to supermartensitic materials; over the last few years (super)duplex materials have suffered from comparable failures. A possibly elegant method might be the application of the moderate cathodic protection (MCP) technique which can guarantee sufficient protection against corrosion as well as avoiding overprotection and the subsequent generation of hydrogen.

5.3 Toughness
Impact tests have so far been the most common way to judge the toughness of supermartensitic materials. It is however known that high strength materials respond differently to dynamic testing than the softer materials do and the results are therefore not necessarily reliable. Several operators have also used CTOD tests, which would give more confidence although for more complicated configurations, tri-axiality effects are not or only partly included. Also the influence of various degrees of cold plastic deformation on the initiation of brittle fractures are not very well known. A more comfortable thought is that the current SMSS alloys display a level of (arbitrary?) toughness that is more than adequate in most cases. Rather than leaning on wide margins of conservatism it would be better to develop a more fundamental understanding of the low temperature behaviour of SMSS alloys.

5.4 Optimisation of welding
From the welding qualification efforts executed so far one may conclude that it is possible to make welds in SMSS materials that exhibit good metallurgical as well as corrosion properties. The main reason to continue welding development work is to weld faster and thus cheaper. The development of chemically matching weld consumables is a very important step towards this goal. For the customary girth welding processes (GTAW, GMAW) there are now consumables available that possess virtually matching mechanical properties to the pipe material. For SAW seam welding the toughness situation is at present more marginal and a considerable effort may be required to achieve a fully satisfactory behaviour of the weld metal. For completeness: various other welding processes have been tried (and some tested), e.g. laser welding electron beam welding, plasma welding, radial friction welding. From all these processes the feasibility is definitely proven but extensive production experience is largely lacking.

5.5 Thin walled pipe making
Recent attempts to produce pipe at a (very) high production rate have highlighted a number of critical aspects. For instance, the coils of SMSS alloys may develop undulations at the edges which may not be manageable by the pipe forming roller system. Also, with the use of fast welding processes as e.g. PAW, Laser welding, EBW, the narrow heating area calls for a very accurate positioning system as missing the seam leads to many defects.

A well developed thin-walled pipe production process could result in a further substantial reduction of the costs whereby even the potential exists that the cost of carbon steel pipes may be approached fairly closely.

5.6 General
The list of issues for further development as mentioned above is certainly not complete. The development of a new family of stainless steels do require a high and continuous level of effort before such materials could be applied in a similar fashion as materials that are already much longer on the market. A serious concern however is that the developments on SMSS materials may get stalled because in the economically tight climate of today insufficient incentives for making the necessary pre-investment may be available in the industry. This situation calls for a high degree of cooperation between all parties in order to make optimal use of the available resources and data, for the benefit of the industry as a whole.

6 Conclusions
- Supermartensitic alloys are well underway in their maturing process: some important open ends however do restrict their application.
- Production aspects of most base materials and products (seamless pipe, plates, SAW pipe, fittings) are well under control.
- Basic pipeline fabrication aspects are now established: there are opportunities for optimisation and significant cost-reduction, e.g. matching consumables, high production welding processes.
- The development of a solution for the prevention of stress corrosion cracking at elevated temperature is well underway but would benefit from a wider support from the industry.
- The influence of hydrogen on supermartensitic alloys and constructions, e.g. sour service resistance, cold deformed material, cathodic protection,
requires thorough attention.

- the development of high productivity pipe production methods can boost the use of supermartensitic alloys.

7 References

1). S Olsen, PE Kvaale, J Enerhaug
   “Experience in the use of EFC-17 for qualification of supermartensitic stainless steel girth welds”
   proc. Supemartensitic Stainless Steels 99 conf., pp 84-87

2). JJ Dufrane, E Franceschetti, J Heather, H van der Winden,
   “Weldable 13%Cr steel: the development of the components for a wet gas piping system”
   Stainless Steel World, April 1999, 27-33

3). P Toussaint, JJ Dufrane
   “Advances in the making and base material properties of supermartensitic stainless steels (SMSS)”
   proc. SMSS 2002 conf., paper 002, Brussels, 2-3 October 2002

4). K Kondo, K Ogawa, H Amaya, H Hirata
   “Alloy design of super 13 Cr martensitic stainless steel”
   proc. SMSS 1999 conf., pp 11-18

5). P Toussaint, H van der Winden
   “Vices and virtues of supermartensitic stainless steels”

6). P Bonnefois, L Coudreuse, P Toussaint JJ Dufrane
   “Developments in GMAW of new martensitic stainless steel”
   proc. SMSS 2002 conf., paper 008, Brussels, 2-3 October 2002

7). V van der Mee, F Neessen
   “Transmission electron microscopy investigation of precipitation reactions in coarse-grained heat affected zone in two 13% Cr supermartensitic stainless steels”
   proc. SMSS 2002 conf., paper 028, Brussels, 2-3 October 2002

8). G Rørvik, PE Kvaale, OM Akselsen
   “Sources and levels of hydrogen in TIG welding of 13%Cr martensitic steels”

9). L Smith, M Celant
   “Martensitic stainless steel pipelines in context”
   proc. SMSS 2002 conf., paper 017, Brussels, 2-3 October 2002

10). E Warren, J Bowers
    “Offshore welding and installation of a weldable 13Cr pipeline”
    proc. SMSS 2002 conf., paper 019, Brussels, 2-3 October 2002

11). M Ueda, H Takabe, K Kondo, K Ogawa, H Hirata, Y Miyazaki
     “Corrosion performance of super 13Cr martensitic stainless steel”
     proc. SMSS 1999 conf., pp 346-352

12). S Olsen
     “Corrosion of SMSS in seawater”
     proc. SMSS 2002 conf., paper 023, Brussels, 2-3 October 2002

13). L Coudreuse, V Ligier, Ch Lojewski
    “Environmental induced cracking (SCC and SCC) in supermartensitic stainless steels (SMSS)”
    proc. SMSS 2002 conf., paper 022, Brussels, 2-3 October 2002

14). T Rogne, M Svenning
     “Intergranular corrosion of supermartensitic stainless steel – A high temperature mechanism?”
     proc. SMSS 2002 conf., paper 024, Brussels, 2-3 October 2002

15). E Ladanova, JK Solberg
     “Moderate cathodic protection and hydrogen embrittlement of supermartensitic stainless steel flowlines”


28). Private communication NAM, October 2001