# STEEL FORGINGS

Second Volume

Edward G. Nisbett and Albert S. Melilli, editors



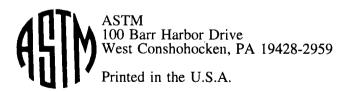
**STP 1259** 

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Edward G. Nisbett and Albert S. Melilli, editors

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The quality of the papers in this publication reflects not only the obvious efforts of the authors and the technical editor(s), but also the work of these peer reviewers. The ASTM Committee on Publications acknowledges with appreciation their dedication and contribution of time and effort on behalf of ASTM.

# **Foreword**

This publication, *Steel Forgings: Second Volume*, contains papers presented at the Second Symposium on Steel Forgings in Hyatt Regency New Orleans, New Orleans, Louisiana, on November 20-21, 1996. The symposium was sponsored by ASTM Committee A-1 on Steel, Stainless Steel, and Related Alloys. The symposium was chaired by E. G. Nisbett, National Forge Company; A. S. Melilli, Consultant, Winchester. They also served as editors of this publication.

# Overview

Steel is supplied in many product forms, most of which are produced in terms of basic dimensions such as width and thickness, or diameter and with length describing quantity. These products may be used by the foot for example as concrete reinforcing bar, or railroad rails or may be fabricated by bending, and welding into products such as storage tanks. Often they essentially lose their identity in the process. Forgings and castings by contrast are diverse in shape and form and are individually made for a specific purpose, either as self contained units such as crankshafts, valve bodies or turbine rotors, or as discrete components to be fabricated into a larger assembly, as for example a nozzle for a pressure vessel. The specification and testing of forgings is therefore more varied, complex, and demanding than is the case for other product forms. This is augmented by the fact that forgings are often expected to give better reliability and service performance than can be expected when the same part is fabricated from sections of other steel product forms, if this were in fact practical. Given these unique circumstances the exchange of ideas on forging manufacturing techniques and experience, materials data and service experience has been an essential driving force in developing forging techniques and applications in every industrial field. In turn these user driven needs and producer developments for manufacture have promoted the development of product specific standards that ASTM, by virtue of its organization capabilities and goals, is able to supply promptly and efficiently. This then was the underlying purpose for both this symposium, and its predecessor held in Williamsburg Virginia in November 1984.

The symposium was sponsored by ASTM Committee A01 on Steel, Stainless Steel, and Related Alloys, and was organized by Subcommittee A01.06 on Steel Forgings and Billets. The symposium was international both in terms of the papers presented and the attendance. The format of the symposium was similar to that of Williamsburg, focusing on the scope of the subcommittee in the areas of pressure vessel and nuclear forgings, turbine and generator forgings, general industrial forgings, and test methods for forgings. Several of these authors who contributed to the first symposium also submitted papers for this the second symposium and so demonstrated an expansion of the developments in their organizations. This was gratifying because time and financial restraints on travel have had a tendency to reduce the exchange of experience and data between those making steel forgings and those who use them—to the detriment of both. Although the maximum benefit will be gained by those who both attended the symposium and obtain this record of the proceedings, it is hoped that this publication extending as it does the published work of the Williamsburg conference will serve as a valuable reference volume for future forging applications.

The keynote address, developed by Mike Gold at very short notice but with keen insight into the current way in which business is being done in the international market, shows that the traditional way of manufacturing equipment in the established industrialized countries and exporting it to the underdeveloped nations is changing to the point that the equipment tends to be built in the destination country itself under a cooperative arrangement. However there is still a niche where critical components, that may possibly include forgings, are made by the more experienced producers.

Although forgings for the domestic commercial nuclear applications are limited to the replacement of items such as steam generators for existing power generating stations, it will

be seen that the development of new manufacturing techniques, such as the forged stainless steel reactor piping units in France that will reduce in service inspection demands and improve component reliability, and the steam generator forging developments in Japan indicate that the nuclear technology continues to progress. Developments intended to improve the mechanical properties of the ASTM A 508 Grade 3 steel, used for many nuclear and other pressure vessel applications, have been described both from domestic and Korean producers, and these may result in revisions to that material grade in A 508, a potential example of specification development through technical exchange. Developments in pressure vessel materials for forgings to be used in high pressure hydrogen environments in the petrochemical industry, and for the manufacture of spent nuclear fuel transportation casks also show how progress is being made in other sections of the pressure vessel industry. The demand for very large and complex components for high temperature catalytic cracker vessels again for the petrochemical industry has spurred material development with consequent material specification revisions.

A potpourri of forging information was included in the General Industrial forging session. This included process model development for the optimization of forging disks, and finite element modeling for open die forging. Both of these papers were from domestic sources, and illustrate the drive to improve forging techniques. A third paper on the forging process this time from China discussed forging hammer force calculation. Sub harmonic treatment of forgings to relieve thermally induced residual stresses and the latest developments in the unique nitrogen alloyed stainless martensitic steels produced in Germany by the pressurized ESR melting process increased the diversity. Other papers in this session also looked at current forging ingot production for the sole remaining domestic producer of very large open die forgings. The manufacture of continuous grain flow crankshafts for medium speed diesel engines is described together with the required materials and properties. The demand for this product has continued to increase, in part because of the use of natural gas for fuel and the potential for high thermal efficiencies when waste heat recovery is included in the installation. Improved toughness grain refined high strength steels for forgings are described in the paper by Leap.

The information given is of a very practical nature and could prove to be useful in specifying heat treatments. The often used sequence of normalizing, quenching, and tempering possibly owes its success to the mechanisms described in that paper. One last area of interest here that could lead to specification revision also was the paper from England on the copper bearing age hardening steels for offshore tension leg platforms. An area of forging problems—all too rarely written about, but none-the-less real was discussed by two very experienced and long time members of the subcommittee. This and their other paper on hydrogen flaking problems—or the apparent lack of them—in forgings gave rise to some spirited discussion which although it does not appear in this account, gave food for thought for those present, and deserves close attention to readers of this volume. The germ of an idea for future papers on failure analysis in forgings came out of these discussions.

Always a source of information on the extremes of forging application the turbine and generator forgings session discussed developments in the martensitic stainless steels for turbine rotors and blades, as well as the combined high pressure—low pressure rotor shafts in a modified 9Cr1Mo high temperature steel. A study in the control of segregation in CrMoV steel ingots for the combined high pressure—low pressure rotors was also presented, both papers coming from Japan. The reader's attention is drawn to the excellent review of the superclean steel forging technology for rotor manufacture that has been spearheaded by EPRI. This steel making practice, made possible by great strides in steel making technology was in its early days at the time of the Williamsburg meeting. It is being

extended to the high temperature pressure vessel field as a way to reduce in service embrittlement.

The steel forgings subcommittee has developed several widely used standards for specialized test methods for forgings, and this subject was covered by two papers on the ultrasonic examination of rotor forgings, one of which is included in this volume. The advantages of being able to record ultrasonic examinations for base reference purposes will spur further activity in this area.

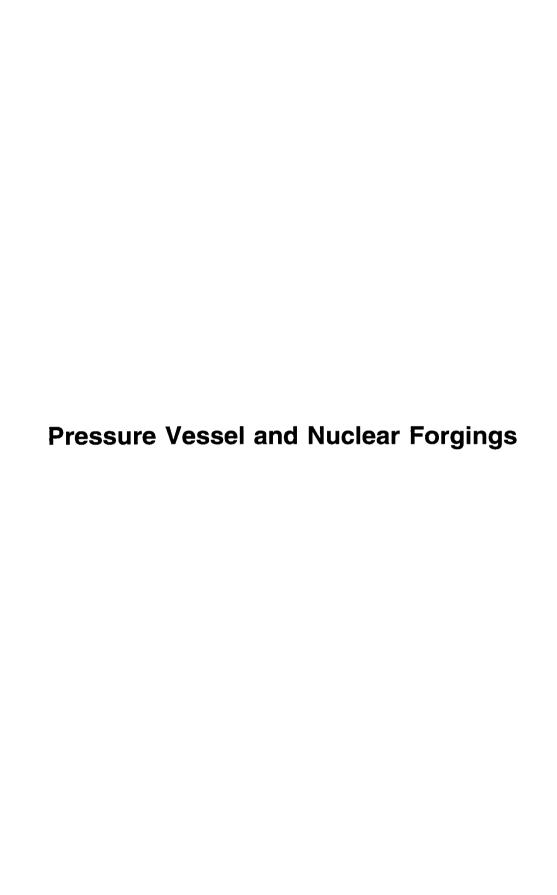
Although forging is an ancient production process long predating the industrial revolution, the development of steel forgings shows no sign of being exhausted, new forging machines continue to appear to make better use of the starting material and reduce cost, and new applications are put forward to meet the expanding needs of industry. Symposia such as this one will assist in obtaining the best from our resources.

Edward G. Nisbett
National Forge Company,
symposium co-chairman and STP editor

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Pierre Bocquet<sup>1</sup>, Alain Cheviet<sup>2</sup>, Lionel Coudreuse<sup>1</sup> and René Dumont<sup>3</sup>

NEW MATERIALS AND FORGINGS USED FOR PRESSURE VESSELS OPERATING IN HYDROGEN ENVIRONMENT

REFERENCE: Bocquet P., Cheviet A., Coudreuse L. and Dumont R., "New Materials and Forgings Used for Pressure Vessels Operating in Hydrogen Environment" <u>Steel Forgings: Second Volume, ASTM STP 1259</u>, E.G. Nisbett and A.S. Melilli, Eds, American Society for Testing Materials, 1997.

ABSTRACT: To improve the in-service behaviour of Cr Mo (V) steel grades used for the pressure vessels operating in hydrogen environment at high temperature for the oil industry, the manufacture of heavy forgings needs a high quality. Improvement of the standard and enhanced strength (ASME Case 1960) 2 1/4 Cr 1 Mo steel grades may be achieved by reducing drastically the impurities (S, P,  $\overline{X}$ , etc ...) to extra low level and avoiding segregates at the inner surface of the shells. For high temperature operation, new V modified steel grades are proposed (ASME case 1961, Code Case 1973 and Code Case 2098). Their conventional mechanical properties are similar to those of enhanced strength 2 1/4 Cr 1 Mo but they offer higher creep properties and improved resistance to hydrogen damage.

**KEYWORDS**: hydrogen damage, pressure vessel, Cr Mo (V) steels, high temperature, embrittlement.

The various high pressure vessels commonly used in the refining oil industry (hydrotreaters, hydrodesulfurisers, hydrocrackers) operating usually at high temperature, high pressure as well as high partial hydrogen pressure are exposed, to several types of damages during their service life.

Made usually from the Cr Mo materials (1.25 Cr - 0.5 Mo, 2 1/4 Cr 1 Mo) those pressure vessels are susceptible to temper embrittlement at operating temperatures (up to 450°C). To estimate this susceptibility to temper embrittlement the mechanical properties of the material are tested in the as heat treated and in post weld heat treated conditions as well as after the step cooling treatment which is supposed to simulate the embrittlement of the material after long term exposure to high temperature.

Furthermore, if locally the temperature happens to rise to a high level, the material can become creep embrittled.

In conversion processes using high hydrogen partial pressure, the materials are exposed to several types of hydrogen damage.

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The most well known damaging mechanism is the hot hydrogen attack which occurs at high service temperature.

Another damage from hydrogen may occur when cooling down the reactor to room temperature, mainly for change of catalyst, due to residual tensile stresses and hydrogen embrittlement. Hydrogen embrittlement has very detrimental effect on the mechanical properties of the material, especially the fracture toughness in the base metal and in the weld metal.

And last, because most of the hydrogen conversion processes contain sulfur acids (H<sub>2</sub>S), the material must be protected against corrosion with a stainless steel cladding. Also, during the cooling down operation the hydrogen content grows at the interface between base metal and the overlay and is a potential source of cracks which creates the disbonding, decohesion of overlay from base metal.

The evolution of in-service temperature and pressure [1] made it necessary to develop improved materials for a better safety of these pressure vessels.

# IMPROVEMENTS TO STANDARD AND ENHANCED STRENGTH 2 1/4 Cr 1 Mo MATERIALS

# Temperature and time effects

The temper embrittlement susceptibility of the 2 1/4 Cr 1 Mo steel grade has for a long time been related to the high detrimental effect of the impurities, Phosphorus, Tin, Antimony, Arsenium, of which P plays the most important role.

 $\overline{X}$  ppm [(10P + 5Sb + 4Sn + As).10<sup>-2</sup>] and J factor (%) [(P+Sn) (Si+Mn) 10<sup>4</sup>] are the most commonly used criteria to evaluate this susceptibility for each heat of steel.

At CLI, we estimate the parameter (P+Sn) as the most significant for the evaluation of long term embrittlement [2]. No significant shift in transition temperature may be expected when P+Sn is lower than 0.010 %.

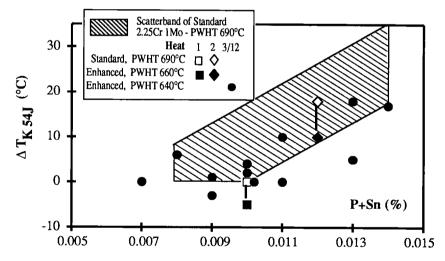


FIG. 1 -- Relationship between  $\Delta T_{K54J}$  and P+Sn for 2 1/4 Cr 1 Mo steels

The scatterband of results of standard 2 1/4 Cr - 1 Mo materials representative of products manufactured at the beginning of the eighties, is compared to data obtained more recently on enhanced 2 1/4 Cr - 1 Mo materials.

It can be concluded that enhanced material does not present higher sensitivity

to temper embrittlement than the standard one.

Temper embrittlement is known to be enhanced in coarse grain area and martensitic microstructure, so it can be expected that in some areas of the heat affected zone (HAZ) of welds, the embrittlement effect is higher.

Tests have been made to evaluate the toughness properties of the HAZ of the stainless steel weld overlay near the fusion line where the grain size number is about 4 (from ASTM E112). The base material had P = 0.006 % and Sn = 0.006 % (P+Sn = 0.012 %).

The results of Charpy test in PWHT condition and after step-cooling are presented in Table 1.

Temperatures in °C	Low PWHT 660°C (Enhanced Material)		Standard PWHT 690°C (Standard Material)	
	Base	HAZ CG	Base	HAZ CG
TK <sub>54J</sub> as PWHT	-90	-90	-87	-90
TK <sub>54J</sub> after S.C.	-80	-56	-69	-79
ΔΤΚ <sub>54J</sub> S.C PWHT	+10	+34	+18	+11
TK + 3 AT	-60	+12	-33	-57

TABLE 1 -- Effect of step cooling and PWHT on Charpy V properties

TK = 54 J transition temperature

It is clear that the PWHT temperature has higher effect on the susceptibility to temper embrittlement of the coarse grain of HAZ than that of base material.

Considering the HAZ of weld seams, we can note that the coarse grain areas are very small and the global properties of these HAZ are not so different from those of base material.

In such welds, it is generally the weld material which presents the lower toughness.

Hydrogen disbonding of the stainless steel weld overlay

Concerning the disbonding phenomenon, extensive investigations have been conducted at CLI's research center (CRMC). Disbonding occurs when the conjunction of hydrogen peak at the interface and of a sensitive microstructure in that area. It has been demonstrated that an increase of carbon content of the interface is a major factor of disbonding sensitivity [3]. So, it is important to control the carbon content at the material surface to be clad as shown in Fig. 2.

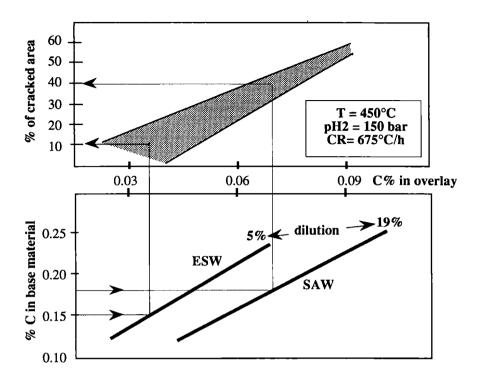


FIG. 2 -- Influence of C content and dilution on disbonding sensitivity

From Fig. 2 it can be noted that, for a carbon content of  $0.15\,\%$  at the weld interface, the disbonding tests give  $10\,\%$  and  $30\,\%$  respectively of cracked area for ESW and SAW weld overlay. In comparison, for areas with C  $0.18\,\%$  ( $20\,\%$  of segregation of carbon) the disbonding tests give  $20\,\%$  and  $40\,\%$  of cracked area respectively for ESW and SAW cladding.

To increase safety margin against that risk of cracking, CLI manufactures its forging shells from hollow ingots which present no segregated areas on the inner surface to be clad by stainless steel weld overlay. [4]

CLI also has developed special forging sequences and techniques to manufacture, special shapes (such as conical, hemispherical shells etc) from hollow ingot in addition to simple shells, to control the carbon content of the inner surface. The photograph (Fig. 3) shows a such element.

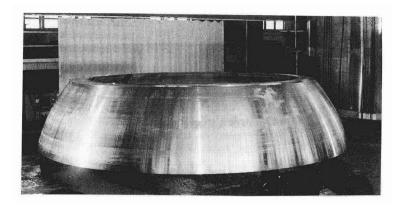


FIG. 3 -- Hemispheric transition ring ("deutchman") manufactured from hollow ingot.

Ø ext 5100 mm - t = 180 mm

### RECENT EVOLUTION OF MATERIALS

Enhanced strength 2 1/4 Cr 1 Mo material (ASME Code Case 1960) is now being used for the reduction of thickness and weight of big pressure vessels operating up to 454°C (850°F). However, to increase the design temperature, it was necessary to develop materials with increased creep resistance compared to the standard or enhanced 2 1/4 Cr 1 Mo and with at least equivalent resistance to hydrogen damages.

The V modified steels developed during the eighties are now being used for the new operating conditions.

The main characteristics of the materials already being used in the industry are given in Table 2.

TABLE 2 -- Steels proposed for pressure vessels in high temperature hydrogen service

Steel grade	Chemical composition	Minimum PWHT	Mechanical properties (MPa)	
	200	temperature	YS	UTS
A336 Cl F22	2.25 Cr 1 Mo	> 675°C	> 310	515/690
Code Case 1960-3		> 650°C	> 380	585/760
A336 Cl. F21B	3 Cr 1 Mo 0.25 V	> 675°C	> 415	585/760
Code Case 1961	Ti B			
Code Case 2098.1	2.25 Cr 1 Mo 0.25 V	> 675°C	> 415	585/760
A336 Cl F91	9 Cr 1 Mo V Nb N	> 730°C	> 415	585/760
Code Case 1973				

# Development of V Modified Cr Mo steels

The 2 1/4 Cr 1 Mo 1/4 V (Code Case 2098) and 3 Cr 1 Mo 1/4 Ti B (Code Case 1961) are new materials with only a short industrial experience and may be considered still under development. At the Vienna Conference in 1994 [5] about ten papers gave a complete view of the situation of these materials which provide allowable stresses similar to the enhanced material but their creep resistance properties allow their use at temperature up to 482°C (900°F).

The 9 Cr 1 Mo V Nb N modified steel (called "grade 91") initially developed for nuclear applications in fast breeder reactors, is largely used in the power plants and petroleum refineries as pipes and tubes. Research work by CLI has shown the interest in such material for future generation of pressure vessels in the oil industry. [6]

CLI has produced industrial heats (up to 190 tons for 3 Cr 1 Mo 1/4 V Ti B material) of all these type of new materials and made an extensive characterization of large components whose results have been published [7] [8]. They confirm the possibility to manufacture these new materials successfully for thicknesses at least up to 300 mm.

Hereafter we shall discuss the two main areas of interest to the fabricator of pressure vessels and the enduser, the weldability and the hydrogen resistance, of these new materials as compared to standard ones.

### WELDABILITY ASPECTS OF NEW MATERIALS

The fabricators of pressure vessels need to control two types of problems associated to the material properties:

- first, they must select welding products and optimize the PWHT conditions to obtain the required mechanical properties of the weld metal and base metal;

- second, they have to avoid the development of cracks in the weld (HAZ and/or Weld Metal) during welding (cold cracking) and during the PWHT (reheat cracking).

For the first question, the choice of PWHT conditions results from a common approach of all concerned parties (fabricator, purchaser of base material, purchaser of welding products). The reason is that the main mechanical properties are directly related to the PWHT conditions (tempering parameter, including time and temperature effects). As an example, the curves of evolution of the tensile properties for V modified 2 1/4 Cr and 3 Cr 1 Mo steels with the tempering parameter TP = T (20+logt) are shown in Fig. 4 and Fig. 5 for both base and weld materials.

To achieve creep properties equivalent to base material, the weld material must contain Nb addition, but that element decreases significantly the toughness properties. [9]. It is clear from Fig. 6 that the properties of submerged arc welds (SAW) are highly dependant of the PWHT condition and the P content. The margin with the required Charpy V-notch level is increased when reducing UTS for a given chemistry. So it is desirable for these materials to optimize the PWHT temperature in the upper range in accordance with the minimum requirement for UTS of base material.

For the V modified 9 Cr 1 Mo steel (grade 91) a similar approach has to be made for optimizing the materials properties [10].

The cracking sensitivity of steels may be evaluated by different testing methods:

The cold cracking sensitivity has been determined by the implant test method in view to define the minimum preheating temperature to avoid cracking. Fig. 7 shows the relation ship between the minimum preheating temperature when applying a stress of 500 MPa to the implant sample and the total hydrogen content of weld metal. The V addition appears to have no significant effect on the risk of cold cracking.