# VALVE

## MAGAZINE

An Introduction
to the 9Cr-1Mo-V Alloys

How to Comply with OSHA's
Ergonomics Program Regulation

Foundry Quality System for
Pressure Vessels in the 21st Century

The "R" Word:
The State of the U.S. Economy

## Making Traffic Flow II:
## Implementing the 'Soft' Side of Lean

The 9Cr-1Mo-V materials are becoming more common as power plant temperatures and pressures are increased to improve efficiencies. The excellent high-temperature properties of the 9Cr-1Mo-V alloys are predicated upon the formation of a particular microstructure containing submicroscopic carbides. The formation of this microstructure is affected by the deoxidation practices used when the alloy is produced, by the heat treatment it receives, and by welding and post-weld heat treatments. If these processes are not properly executed, acceptable creep properties will not be realized even though the composition and room-temperature mechanical properties will appear acceptable.
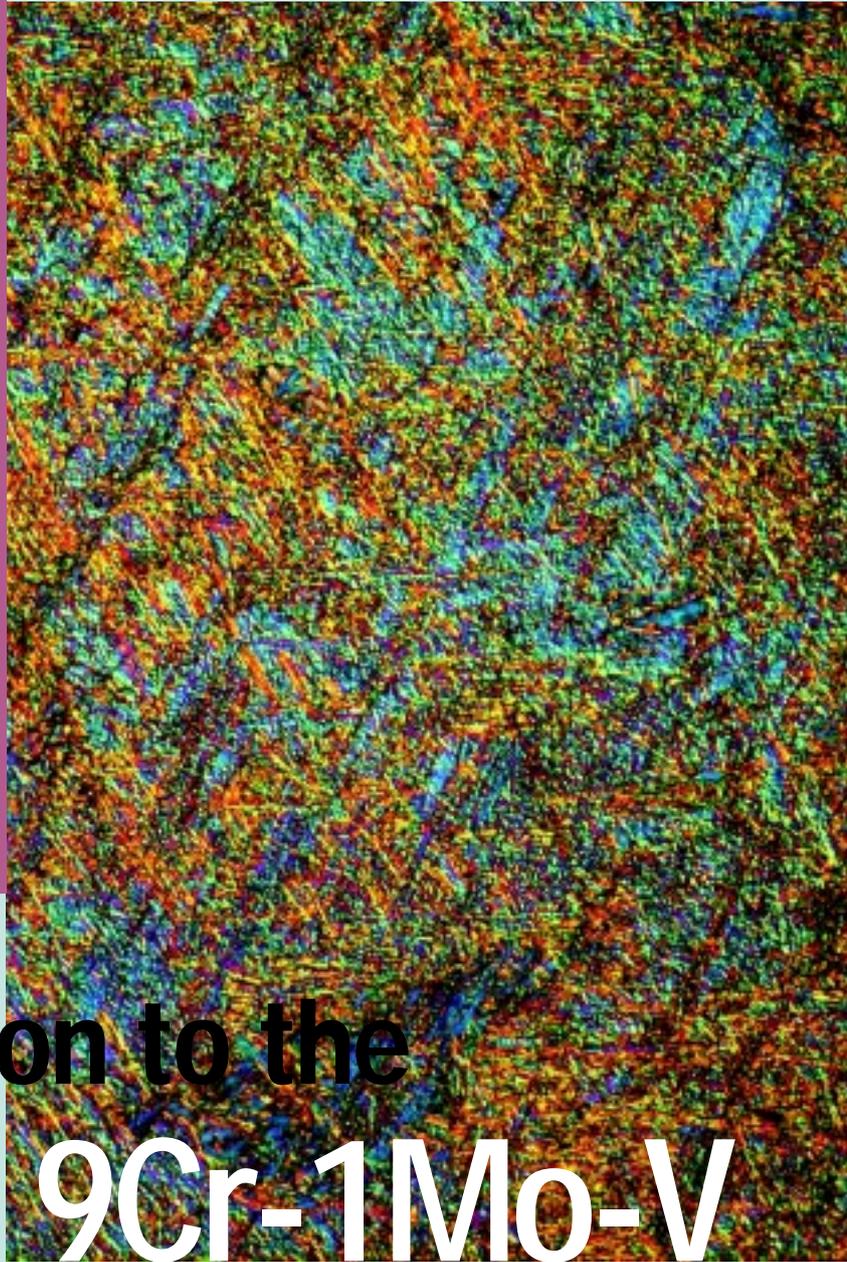
# An Introduction to the 9Cr-1Mo-V ALLOYS

DONALD R. BUSH

T he pursuit of improved efficiency and reduced emissions in power plants has resulted in the design of systems utilizing higher and higher steam temperatures and pressures. This shift to higher temperatures requires the use of materials with appropriate high-temperature strength, creep properties, physical properties, and metallurgical stability at the operating temperature of the unit to prevent catastrophic failures by several potential long-term mechanisms, including leakage due to creep-induced dimensional changes, bursting due to stress rupture, or thermal fatigue due to thermally-induced cyclic stresses.

In the 1970s, Oak Ridge National Laboratory developed a new alloy system, commonly referred to as 9Cr-1Mo-V, that provides excellent elevated-temperature properties.[1] The use of this alloy in various forms has accelerated significantly in the past few years as new power plants are being built. This article discusses the general characteristics of the alloy, the applicable specifications and grade names, and some of the technical issues involved in its use.

## THE ALLOY SYSTEM

Austenitic stainless steels have commonly been used for high-temperature steam applications due to their excellent strength retention at high temperatures. However, there are drawbacks to their use. In addition to their relatively high cost, the austenitic stainless steels exhibit high thermal expansion rates and low thermal conductivity. This results in the development of high thermally-induced stresses during heating and cooling, which can cause thermal fatigue.

The modified alloy system is similar to the conventional 9Cr-1Mo (9% chromium, 1% molybdenum) grades. Modifications include additions of vanadium, niobium (sometimes called columbium), and nitrogen, as well as a lower carbon content. When produced and heat treated to form the proper microstructure (See "The Importance of Microstructure" on

| Table 1 – ASTM and ASME Specifications and Grades for 9Cr-1Mo-V Materials | | | |
|---|---|---|---|
| Form | ASTM | ASME | Grade Designation |
| Forging | A182 | SA182 | F91 |
| Seamless Tubing | A213 | SA213 | T91 |
| Seamless Pipe | A335 | SA335 | P91 |
| Forged Pipe | A369 | SA369 | FP91 |
| Plate | A387 | SA387 | Grade 91 |
| Piping Fitting | A420 | SA420 | WP91 |
| Forging | A336 | SA336 | F91 |
| Casting | A217 | Code Case 2192-2 | C12A |

| Table 2 – Compositions for Various Forms | | | |
|---|---|---|---|
| Element | Wrought Grades F91, T9, WP91, P91, F91, and 91 | Cast Grade C12A | Castings per ASME Code Case 2192-2 |
| C | 0.08-0.12 | 0.08-0.12 | 0.08-0.12 |
| Mn | 0.30-0.60 | 0.30-0.60 | 0.30-0.60 |
| P | 0.020[a] | 0.020 | 0.020 |
| S | 0.010[a] | 0.010 | 0.010 |
| Si | 0.20-0.50 | 0.20-0.50 | 0.20-0.50 |
| Cr | 8.00-9.50 | 8.0-9.5 | 8.00-9.50 |
| Mo | 0.85-1.05 | 0.85-1.05 | 0.85-1.05 |
| Ni | 0.40 | 0.40 | 0.40 |
| V | 0.18-0.25 | 0.18-0.25 | 0.18-0.25 |
| N | 0.030-0.070 | 0.030-0.070 | 0.03-0.07 |
| Nb (Cb) | 0.06-0.10 | 0.060-0.10 | 0.06-0.10 |
| Al | 0.04 | 0.040 | 0.02 |
| Ti | --- | --- | 0.005 |

[a] 0.025 in ASTM A336 and ASME SA336

| Table 3 – Mechanical Property Requirements for Various Forms | | | |
|---|---|---|---|
| | Specification/Grade | | |
| Property | A182/SA182 F91 A213/SA213 T91 A335/SA335 P91 A387/SA387 Gr 91 | A217 C12A | ASME Code Case 2192-2 Castings |
| Minimum Ultimate Tensile Strength, ksi (MPa) | 85 (585)[a] | 85 (585)[a] | 85 (585) |
| Minimum Yield Strength, ksi (MPa) | 60 (415) | 60 (415) | 60 (415) |
| Minimum % Elongation | 20[b] | 20 | 20 |
| Minimum % Reduction in Area | 40 (SA182) | 45 | --- |
| Maximum Hardness, HB | 248 (SA182) | --- | --- |

[a] SA217, SA234 and SA387 include a maximum tensile strength requirement of 110 ksi (760 MPa)
[b] Minimum elongation per SA387 is 18%

page 8), this alloy provides extremely good mechanical properties at elevated temperatures. In addition, because of its lower thermal expansion coefficient and higher thermal conductivity, the alloy is much more resistant to thermal fatigue than the austenitic stainless steels.

## SPECIFICATIONS AND GRADES

9Cr-1Mo-V materials have been adopted in various forms in a number of ASTM/ASME standards, and many are listed in the ASME Boiler and Pressure Vessel Code Section II Part D allowable stress tables with a maximum temperature rating of 649°C (1200°F). The standards and grade designations for various forms are shown in **Table 1**. Compositions, mechanical properties, and ASME allowable stresses are listed in **Tables 2, 3, and 4**. Note that these materials do not provide any major benefit over more conventional materials such as F22 or WC9 for use below about 900°F (482°C), but that they provide much higher allowable stresses in the range from 900-1100°F (482-593°C).

## PROCESSING ISSUES

Because it is critical that a specific microstructure be present in order to realize the high-temperature properties[1], there are a number of metallurgical issues that must be addressed with respect to deoxidation practices, heat treatment, and welding processes used in the production of the material.

## DEOXIDATION

During the production of raw material or castings, consideration must be given to the deoxidation practice used to tie up dissolved oxygen in the molten metal prior to pouring ingots or castings. Deoxidation is generally accomplished by adding small quantities of elements which have a high affinity for oxygen, a practice commonly referred to as "killing" in

conjunction with wrought products. These elements combine with the oxygen to form solid oxide inclusion particles, preventing the formation of gas porosity in the ingot or casting. The most common deoxidizers are manganese, silicon and aluminum, although many other elements with high oxygen affinity, including titanium, zirconium, niobium, magnesium, and calcium might be utilized.

The deoxidation practice is critical in the 9Cr-1Mo-V materials because of the presence of nitrogen and the purpose it serves in creating a proper microstructure (See "The Importance of Microstructure" on page 8). Many of the elements used for deoxidation also have a high affinity for nitrogen. If certain deoxidizing elements are utilized, or are simply present in the melt as residuals in high enough quantities, they can effectively tie up the nitrogen, and it won't be available during heat treatment to form the fine niobium carbonitrides. When this happens, large, blocky carbide phases will form instead. Without the fine niobium

| Table 4 - ASME Boiler and Pressure Vessel Code Section II Part D Allowable Stresses (ksi) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Castings | | | | Wrought | | | | |
| Temperature, °F (°C) | WC9 | C12 | Cast 9Cr-1Mo-V[a] | CF8M | F22 | F9 | F91 ≤ 3" | F91 > 3" | S31600 |
| 100 (38) | 20.0 | 25.7 | 21.3 | 20.0 | 21.4 | 24.3 | 24.3 | 24.3 | 20.0 |
| 200 (93) | 20.0 | 25.7 | 21.3 | 20.0 | 21.4 | 24.2 | 24.3 | 24.3 | 20.0 |
| 300 (149) | 19.7 | 24.9 | 20.6 | 19.4 | 20.9 | 23.5 | 24.3 | 24.3 | 19.4 |
| 400 (204) | 19.4 | 24.7 | 19.9 | 19.2 | 20.6 | 23.4 | 24.2 | 24.2 | 19.2 |
| 500 (260) | 19.3 | 24.6 | 19.3 | 17.9 | 20.5 | 23.3 | 24.1 | 24.1 | 17.9 |
| 600 (316) | 19.2 | 24.3 | 18.7 | 17.0 | 20.4 | 22.9 | 23.7 | 23.7 | 17.0 |
| 650 (343) | 19.1 | 23.9 | 18.4 | 16.6 | 20.2 | 22.6 | 23.4 | 23.4 | 16.6 |
| 700 (371) | 18.8 | 23.4 | 18.1 | 16.3 | 20.0 | 22.1 | 22.9 | 22.9 | 16.3 |
| 750 (399) | 18.5 | 22.7 | 17.7 | 16.0 | 19.7 | 21.4 | 22.2 | 22.2 | 16.1 |
| 800 (427) | 17.9 | 21.8 | 17.2 | 15.8 | 19.3 | 20.7 | 21.3 | 21.3 | 15.9 |
| 850 (454) | 17.2 | 20.8 | 16.7 | 15.7 | 18.7 | 19.7 | 20.3 | 20.3 | 15.7 |
| 900 (482) | *15.8* | *16.4* | 16.1 | 15.5 | *15.8* | *16.4* | 19.1 | 19.1 | 15.6 |
| 950 (510) | *11.4* | *11.0* | 15.5 | 15.4 | *11.4* | *11.0* | 17.8 | 17.8 | 15.4 |
| 1000 (538) | *7.8* | *7.4* | 14.3 | *14.9* | *7.8* | *7.4* | 16.3 | 16.3 | 15.3 |
| 1050 (566) | *5.1* | *5.0* | 11.4 | *11.5* | *5.1* | *5.0* | 14.0 | 12.9 | 15.1 |
| 1100 (593) | *3.2* | *3.3* | 8.8 | *8.9* | *3.2* | *3.3* | 10.3 | 9.6 | *12.4* |
| 1150 (621) | *2.0* | *2.2* | 6.5 | *6.9* | *2.0* | *2.2* | 7.0 | 7.0 | *9.8* |
| 1200 (649) | *1.2* | *1.5* | 4.2 | *5.4* | *1.2* | *1.5* | 4.3 | 4.3 | *7.4* |
| 1250 (677) | | | | *4.3* | | | | | *5.5* |
| 1300 (704) | | | | *3.4* | | | | | *4.1* |
| 1350 (732) | | | | *2.8* | | | | | *3.1* |
| 1400 (760) | | | | *2.3* | | | | | *2.3* |
| 1450 (788) | | | | *1.9* | | | | | *1.7* |
| 1500 (816) | | | | *1.6* | | | | | *1.3* |

[a] *Allowable Stresses from ASME Code Cases 2192-2. Values should be acceptable for ASTM A217 C12A.*
*Note: Section II Part D indicates values in italics are based upon time-dependent properties.*

carbonitrides, the submicroscopic, high-vanadium $M_{23}C_6$ particles will not form, and the material will not possess the required high-temperature properties. Therefore, a proper deoxidation practice must be used to ensure that the alloy will perform as intended.

## HEAT TREATMENT

Although the normalizing portion of the heat treatment does not require extremely tight control[1], the subsequent tempering procedure is critical to the formation of the proper microstructure. The presence of vanadium and niobium makes the alloy very resistant to softening at normal tempering temperatures. As a result, these alloys are generally tempered at 1375-1420°F(745-770°C), even though the ASTM and ASME specifications only require a minimum tempering temperature of 1350°F (730°C). A target temperature of 1400°F (760°C) is generally recommended in the technical literature to provide an optimum combination of strength, creep resistance, and impact toughness.

Temperature control during the tempering phase is critical, especially with regard to the maximum temperature attained. Depending upon the concentration levels of various elements, especially nickel and manganese, the lower critical temperature (where austenite begins to re-form) can fall to below 1500°F (815°C). If adequate temperature controls are not utilized during the tempering heat treatment, it is possible to form fresh austenite or ferrite during the tempering process. Upon cooling, any fresh austenite will convert to untempered martensite. The presence of either ferrite or untempered martensite will compromise both the toughness and high-temperature properties of the material. Thus, strict temperature controls during this heat treatment phase are critical, and care must be taken to ensure that the temperature does not overshoot during the heat-up portion of the cycle.

## WELDING

There are a number of factors that make welding and post-weld heat treatment (PWHT) of this alloy complex. The high alloy content provides very high hardenability, which means that martensite will form readily in the weld and heat affected zone (HAZ) even upon slow cooling. On the other hand, the relatively low carbon content limits the hardness that is attained in the martensite. Thus, the alloy has inherently better weldability than the conventional 9Cr-1Mo materials with higher carbon contents, which generally develop higher hardnesses.[2]

All forms other than castings are classified as P-5B Group 2 materials in Section IX of the ASME Boiler and Pressure Vessel Code. Castings have not been assigned a P-number, although Code Case 2192-2 states that castings should be treated as P-5B Group 2 materials for the purpose of PWHT.

ASME B31.3 (Process Piping Code) requires a preheat of 350°F (175°C) whereas ASME B31.1 (Power Piping Code) and the ASME Boiler and Pressure Vessel Code require a 400°F (200°C) preheat. It is generally recommended in the literature that a minimum preheat of 400°F (200°C) be applied, and that the interpass temperature be limited to a minimum of 400°F (200°C) to prevent cold cracking and a maximum of 575°F (300°C) or 600°F (315°C) in order to prevent hot cracking and to allow each pass to at least partially transform to martensite prior to the start of the next pass.[3]

There are a number of weld filler options, some which fall under industry standard specifications and some which are proprietary. The 9Cr-1Mo-V filler material grades and compositions from ASME specifications are listed in *Table 5*. Various filler compositions have been developed due to the large number of compositional factors that affect weld metal

| Table 5 – Compositions of Weld Filler Materials | | | |
|---|---|---|---|
| Element | ASME SFA-5.28 (GTAW, GMAW, PAW) | ASME SFA-5.23 (SAW) | ASME SFA-5.5 (SMAW) |
| C | 0.07-0.13 | 0.07-0.13 | 0.08-0.13 |
| Mn | 1.25 | 1.25 | 1.25 |
| P | 0.010 | 0.010 | 0.010 |
| S | 0.010 | 0.010 | 0.010 |
| Si | 0.15-0.30 | 0.30 | 0.30 |
| Cr | 8.00-9.50 | 8.00-10.00 | 8.00-10.50 |
| Mo | 0.80-1.10 | 0.80-1.10 | 0.85-1.20 |
| Ni | 1.00 | 1.00 | 1.00 |
| V | 0.15-0.25 | 0.15-0.25 | 0.15-0.30 |
| N | 0.03-0.07 | 0.03-0.07 | 0.02-0.07 |
| Nb (Cb) | 0.02-0.10 | 0.02-0.10 | 0.02-0.10 |
| Al | 0.04 | 0.04 | 0.04 |
| Cu | 0.20 | --- | 0.25 |
| Total Other | 0.50 | --- | --- |

| Table 6 – ASME Code PWHT Requirements | | |
|---|---|---|
| Code | PWHT Temperature | Shortest PWHT Time Allowed |
| ASME B&PV Code Section VIII Div 1 | 1300°F (704°C) minimum | 15 minutes |
| ASME B31.1 Power Piping Code | 1300-1400°F (704-760°C) | 15 minutes |
| ASME B31.3 Process Piping Code | 1300-1400°F (704-760°C) | 2 hours |

properties. Higher nickel content promotes better impact toughness, but also tends to reduce the lower critical temperature. Most filler material compositions allow a higher percentage of nickel than is allowed in the base metal. However, the sum of nickel + manganese must be controlled to ensure that the lower critical temperature does not encroach upon the PWHT temperature range. Niobium, vanadium, and nitrogen promote creep resistance, but reduce toughness. Silicon is necessary for deoxidation, but is detrimental to impact properties. The various available filler materials are formulated to produce slightly different combinations of creep resistance and toughness. Selection of filler material depends upon the desired end properties.

The ASME Boiler and Pressure Vessel Code, ASME B31.1, and ASME B31.3 PWHT temperature and time requirements are listed in *Table 6*. Note that the ASME Boiler and Pressure Vessel Code and ASME B31.1 allow PWHT temperatures as low as 1300°F (704°C) and times as short as fifteen minutes. PWHT at temperatures this low will not adequately temper the weld filler materials due to their higher nickel and manganese contents. PWHT should be conducted at a minimum of 1365°F (740°C), and a target temperature of 1400°F (760°C) is generally considered optimum. The alloy system responds slowly to tempering treatments because of its excellent high-temperature stability. As a result, the PWHT duration should never be less than two hours, even though the ASME codes allow PWHT for times as short as fifteen minutes in thinner sections.

Because of the high hardenability of these materials, there are some precautions that must be considered during the actual fabrication. Because the most recently deposited metal is fully martensitic, it is very susceptible to brittle fracture if overstressed. Therefore, care must be taken when lifting and handling the weldment, or when welding is interrupted *(i.e., if the weldment is allowed to cool to below the preheat temperature)* prior to completion of the joint. Under ideal conditions, the entire joint should be completed without interruption. If this is not possible, at least 1/3 of the joint should be completed before interruption is allowed. Cooling and re-preheating should be performed slowly to prevent thermal stresses.

ASME/ANSI B31.1 includes some specific verbiage regarding interruption of welding. To briefly summarize the main points, the preheat temperature must be maintained until any required PWHT is performed, unless certain conditions are satisfied. Those conditions are:

• At least 3/8" or 25% of the welding groove must be filled (whichever is less);

• The weldment must be subjected to an intermediate heat treatment with a controlled rate of cooling (this intermediate heat treatment is not defined);

• After cooling and before welding is resumed, visual examination must be performed to ensure no cracks have formed;

• Required preheat must be applied before welding is resumed.

## CASTINGS

The development of a cast material often lags a number of years behind the development of its wrought counterpart. C12A, the 9Cr-1Mo-V cast grade, is no exception. Although the 9Cr-1Mo-V materials were developed in the mid-1970s, cast 9Cr-1Mo-V did not appear in a North American industry standard until 1995, when ASME Code Case 2192 was issued. C12A was added to ASTM A217 later in 1995. ASME still has not adopted C12A into the SA217 specification. ASME has re-approved Code Case 2192 twice, the most recent being version 2192-2 in October of 1999.

Specific requirements for the cast version are still being actively developed in the ASTM and ASME standards committees. Put simply, it is quite possible to produce cast material that meets all of the industry-standard chemical and mechanical property requirements for C12A, but which does not provide the excellent high-temperature strength and creep resistance that is necessary for the intended use. None of the ASTM or ASME specifications contain adequate chemistry requirements to ensure proper deoxidation practices will be followed. Even the ASME Code Case 2192-2 composition, with its tighter aluminum restriction and additional titanium restriction, does not ensure that other elements with high nitrogen affinity *(zirconium, for example)* will not be utilized. Unless this issue has been specifically communicated, it's likely that many foundries will be unaware of the effect that deoxidation practices can have on the high-temperature properties. In fact, there is a good chance that extra killing agents might be added to counteract the potential for the nitrogen to outgas and cause porosity in the casting.

There are several approaches that could be considered to ensure that the material has been produced properly in order to meet the actual requirements of the application:

• Creep testing could be performed to verify long-term properties at the intended service temperature. The drawback to creep test verification is that it takes too long. A 10,000-hour creep test, which can be used to predict 100,000-hour performance, takes nearly fourteen months. Therefore, this approach is not practical for verification of products.

• Microstructural examination has been suggested, and

would actually serve two purposes. The lack of large, blocky carbides would verify that the nitrogen was available to ensure the formation of the niobium carbonitrides, verifying that proper deoxidation had occurred. The lack of ferrite or untempered martensite would verify that heat treatment had been performed properly. ***See Figures 1 and 2***. However, there are drawbacks to this approach. The thickest and thinnest sections experience different heating and cooling rates, and can even experience different maximum temperatures during heat treatment. This makes it difficult to write a general requirement that states how the sampling should be performed to produce microstructural examination results that truly represent all sections in the casting. Examination of a section of the casting riser immediately adjacent to the casting itself has been suggested. This location essentially represents the thickest section in the casting. However, most foundries remove the riser and other rigging prior to heat treatment, so a requirement of this nature forces the casting into "special processing", which automatically increases the cost and delivery lead-time. In addition, this approach might not identify overheating in a thin section of a casting due to a brief furnace overshoot.

• Explicit limitations on nitrogen-forming elements could ensure that killing agents with a high affinity for nitrogen would not be utilized. The aluminum and titanium restrictions listed in ASME Code Case 2192-2 are based upon this concept. Unfortunately, there are a number of elements other than aluminum and titanium that also have high nitrogen affinities. It has recently been suggested that a general statement be added to ASTM A217 regarding restrictions on deoxidizing agents for C12A castings. The proposed requirement would prohibit the use of any element which forms a nitride at 1500°C (2730°F) at a lower free energy of formation than that of niobium nitride. This would ensure that the nitrogen in the alloy would combine more readily with niobium than with any of the other elements in the alloy. The proposed revision would allow the use of silicon, calcium, vanadium, chromium, molybdenum, lithium, barium, or magnesium, but would prohibit the use of aluminum, zirconium, titanium, tantalum, thorium, or boron. This approach seems to provide a straightforward requirement that ensures the development of the required properties. It is assumed that actual upper limits would need to be defined for each of the prohibited elements.

Until the time when ASTM or ASME adopts one of these approaches, supplementary controls should be imposed by the purchaser to ensure that castings will possess the creep resistance required for high-temperature use.
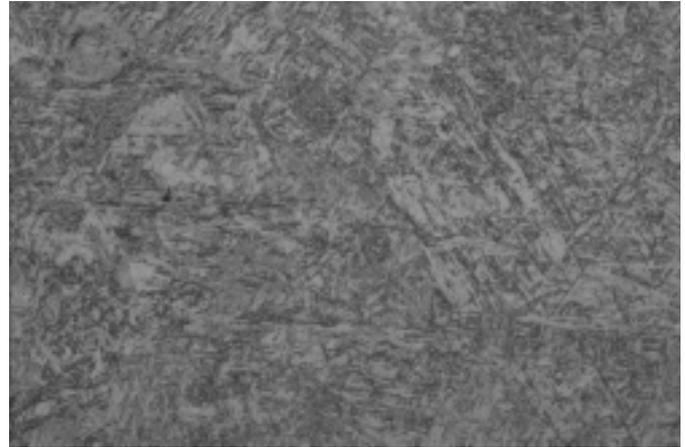


*Figure 1: Proper microstructure in a 9Cr-1Mo-V casting. Note the lack of ferrite or blocky carbide phases. Original magnification: 100X*
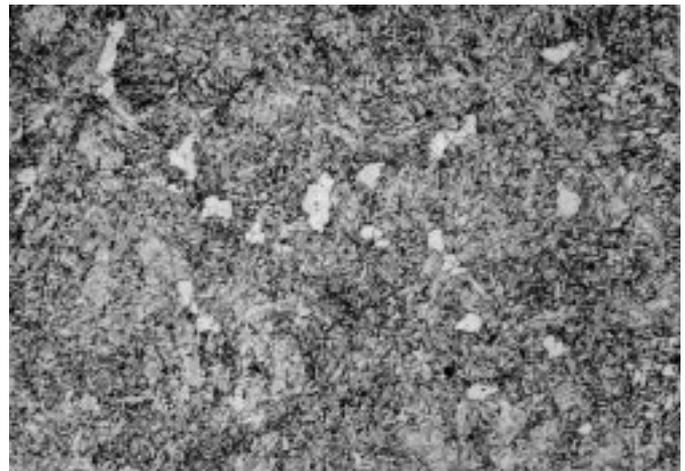


*Figure 2: Improper microstructure in a 9Cr-1Mo-V casting. Note the presence of ferrite (white islands). Original magnification: 200X*

## SUMMARY

The use of 9Cr-1Mo-V alloys is on the rise. When produced and processed properly, these alloys exhibit properties that make them attractive for use in place of austenitic stainless steels for high-temperature steam applications. However, if the materials are not properly melted and refined, heat treated, welded, and post-weld heat treated, the desired high-temperature properties will not be realized. Strict attention must be paid to these details when building equipment in order to avoid catastrophic failures after extended service at high temperatures.

*The author is Senior Engineering Specialist, Materials Engineering Department, Fisher Controls International, Inc., Marshalltown, IA; 641.754.3011; www.frco.com.*

[1] "Development of Modified 9 Cr-1 Mo Steel for Elevated-Temperature Service", Vinod K. Sikka.

[2] "Guideline for Welding P(T)91", William F. Newell, Jr., Euroweld, Ltd.

[3] "European State of the Art of Modified 9% Cr Steels: Welding, Fabrication and Industrial Applications of P91/T91 and New Developments", C. Coussemen, S. Huysmans, E. Van Der Donckt, C. Verscelden, EPRI Conference Proceedings, June 1998.

## THE IMPORTANCE OF MICROSTRUCTURE

The chemistry of the 9Cr-1Mo-V material is specially designed to support the formation of a microstructure which provides excellent long-term high-temperature strength, creep and stress rupture properties.

When the material is normalized by air-cooling from a target temperature of 1900°F (1040°C), a completely martensitic structure with a hardness of approximately 35-40 HRC is formed.

Tempering at the target temperature of 1400°F (760°C) softens the martensite and ultimately produces a hardness on the order of 95 HRB. However, in addition to the conventional tempering effects, a secondary precipitation process also occurs. The first stage of this process involves the precipitation of very fine Nb(C,N) (niobium carbonitride) particles. The Nb(C,N) particles subsequently act as nucleation sites for the formation of very fine particles of $M_{23}C_6$.[1] $M_{23}C_6$ is metallurgical shorthand for a carbide structure containing a mixture of 23 Metal atoms and 6 Carbon atoms. The 23 metal atoms are generally rich in the alloy's stronger carbide-forming elements such as chromium, vanadium, niobium, etc.

Research on the 9Cr-1Mo-V material indicates that the $M_{23}C_6$ phase contains an appreciable amount of vanadium, which makes it very stable at the intended service temperature. This stability mitigates growth and consolidation of the $M_{23}C_6$ particles in service.[1]

Since high-temperature strength and creep resistance are enhanced by the presence of large quantities of very small particles, both the initial precipitation of Nb(C,N) and the subsequent formation of stable submicroscopic vanadium-rich $M_{23}C_6$ particles are key elements contributing to the long-term performance of this alloy.

D350827X012