Metallurgical Considerations in the Manufacture of Clad Heads

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ABSTRACT

Manufacture of clad pressure vessels frequently requires elevated temperature forming of heads. For some clad metal combinations, there are conflicts between the ideal hot metal working parameters for the cladding metal and base metal. Further, bi-metal interactions of some metal combinations at elevated temperatures can result in significant deterioration of interface strength and ductility. Improper forming conditions can result in loss of cladding metal corrosion properties, inappropriate base metal mechanical properties, and/or clad separation. NobelClad has extensive experience with the conventional clad metal combinations and has established forming parameters which result in reliable corrosion resistance of the cladding metal, Code compliant base metal, and absence of interface problems. Critical issues and concerns are discussed and case histories and test results from representative clad head forming projects are presented.

KEYWORDS

Clad, sensitization, elevated temperature forming, head forming, stainless steel, nickel alloys, titanium, zirconium, PWHT, heat treatment, fabrication.

INTRODUCTION

Clad material usage has grown significantly over the past 40 years, and today clad materials are employed in varied and diverse applications. Most of these applications require that the clad material be formed during fabrication; and forming of the heads may be the most demanding aspect of fabrication due to the need to achieve the required head shape tolerances without compromising the clad physical and mechanical properties. For vessel heads, the base metal is typically a pressure vessel quality steel such as SA516 or SA387 and is selected based on code design requirements, fabrication characteristics and mechanical properties. The cladding metal is generally for "corrosion allowance only" and may be selected from a wide range of stainless steels, nickel alloys or reactive metals. The primary consideration in forming of clad heads is insuring all of the ASME Code requirements are met to assure pressure vessel integrity. UG-79 states: "All plates for shell sections and for heads shall be formed to the required shape by any process that will not unduly impair the physical properties of the material." UG-32, UG-33 cover formed head design requirements, and UG-81 defines dimensional tolerances. [1-4]

Typical head forming processes include dishing and flanging, spinning, and pressing. Each of these processes may be performed over a range of temperatures. When discussing metallurgical considerations it is useful to classify the forming process as cold forming, warm forming or hot forming.

The term cold forming or cold working is applied to deformation conducted at ambient shop temperatures or with only low temperature preheat (up to ~260°C). At these temperatures, the primary metallurgical consideration is work hardening. During cold forming the hardness, ultimate tensile and yield strength increase while the ductility falls to a lower value. UCS-79 provides limits on cold working of carbon and low alloy steel materials and defines when subsequent heat treatment is required (UCS-56). [5,6] For cold forming, the critical material properties are yield strength, ductility and toughness. For clad materials this includes the bond interface strength and toughness. The yield strength determines forming loads and springback, and the material must have the ductility and toughness to allow the deformation necessary to achieve head dimensional tolerances without cracking or bond separation.

Warm forming can be defined as forming at elevated temperatures, but below the lower critical temperature for steels, and generally below temperatures that result in the formation of secondary phases (~480 - ~700°C). Increasing the temperature of the formed part reduces the forming loads and can be helpful in difficult forming applications where hot forming may not be possible due to material instability or detrimental interfacial reactions. Depending on the alloy, forming temperature and extent of deformation, the grain structure may or may not recrystalize during forming. Because of the possible changes in mechanical properties with exposure to elevated temperatures, UCS-85 provides requirements (with some exemptions) for heat treatment of test specimen that includes "all thermal treatments of the material during fabrication exceeding 900°F" (482°C). [7]

Hot forming or hot working of clad steel is deformation conducted in the austenitic region above the upper critical temperature (~ 870+ °C). During hot working, deformation of the grains is followed immediately by recrystallization so that the effects of deformation on the structure and properties are removed.[8] Hot forming allows a significant reduction in forming loads due to the reduction in yield strength at these temperatures, and for applications with thick or high strength materials hot forming of the heads is required. However, exposure of clad materials to these higher temperatures may lead to significant changes in microstructure and mechanical properties. For some clad metal combinations, there are conflicts between the ideal

hot metal working parameters for the cladding metal and base metal. Further, bi-metal interactions of some metal combinations at elevated temperatures can result in significant deterioration of interface strength and ductility. Improper forming conditions can result in deterioration of cladding metal corrosion properties, non-compliant base metal mechanical properties, and/or clad separation.

Table 1 summarizes the clad materials for which forming procedures have been developed and used extensively by NobelClad. Metallurgical considerations for each group are discussed below.

Cladding Metals	Base Metals
Austenitic Stainless Steels and Nickel Alloys	Carbon and Alloy Steels, 3xxL Stainless Steels
410S and Duplex Stainless Steels	Carbon and Alloy Steels
Titanium and Zirconium	Carbon and 3xxL Stainless Steels
Tantalum	Carbon and 3xxL Stainless Steels

TABLE 1: CLAD MATERIALS WITH HEAD FORMING EXPERIENCE AND FORMING PROCEDURE DEVELOPMENT

AUSTENITIC STAINLESS STEEL AND NICKEL ALLOY CLAD

The austenitic stainless steels and nickel alloys are characterized by good ductility and formability, good low temperature toughness, but a relatively high work hardening rate. These alloys form a strong, tough bond with carbon and alloy steel base materials and the bond is not weakened or embrittled by exposure to elevated temperatures. As a result, these clad materials may be formed over the entire forming temperature spectrum without risk of clad separation. These alloys may be readily cold formed, but consideration should be given to their high work hardening rate.

The primary consideration in forming these materials is degradation of the cladding metal corrosion properties. During elevated temperature forming, the cladding metal may become sensitized by the precipitation of secondary phases. These phases may be classified as carbides, nitrides and intermetallic compounds. The more important secondary phases that occur in these alloys are shown in Table 2. [9] The extent to which these phases occur depends on actual chemistry, segregation effects and thermal-mechanical treatments. The alloying elements that improve corrosion resistance, nickel, chromium and molybdenum, participate in the formation of many of these phases. The mechanism of "sensitization" is well documented, and in general is not caused by attack of the secondary phase, but instead is caused by alloy depletion in the adjacent regions. [10] Precipitation of deleterious phases frequently occurs at grain boundaries leading to intergranular sensitization, but secondary phases may also precipitate within the matric and reduce pitting resistance.

Phase	Type/Formula	Temperature Range	Structure
Chromium Carbide	$(Cr,Fe,Mo)_7C_6$	950 - 1050° C	Orthorhombic
Chromium Carbide	$(Cr,Fe,Mo)_{23}C_6$	600 – 950° C	Cubic
Chromium Carbide	$(Cr,Fe,Mo,Cb)_6C$	600 – 950° C	Cubic
Chromium Nitride	$(Cr,Fe)_2N$	650 – 950° C	Hexagonal
Sigma σ	(Cr,Fe,Mo,Ni)	550 – 1050° C	Tetragonal
Chi x	$Fe_{36}Cr_{12}Mo_{10}$	600 – 900° C	Cubic
Laves n	$(FeCr)_2(Mo,Nb,Ti,Si)$	550 – 900° C	Hexagonal

TABLE 2: SECONDARY PHASES IN STAINLESS STEELS AND NICKEL ALLOYS[9]

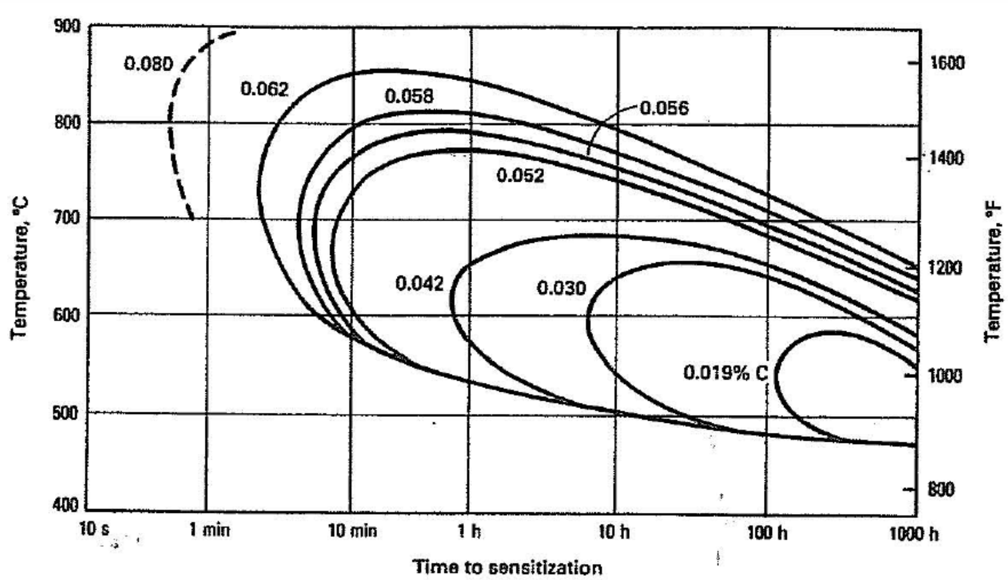
The rate of formation of secondary phases can be very rapid. Consequently, the head forming procedure must take reaction kinetics into account to ensure that anticipated corrosion resistance is obtained. Time-Temperature-Sensitization (TTS) diagrams are employed to evaluate the forming window. In actual practice, the heating/cooling cycles are not isothermal and exposure is minimized by limiting hold times. Therefore the isothermal TTS curves are somewhat conservative. For typical hot forming cycles, the time at temperature is ~1-3 hrs, but as the clad material thickness and forming difficulty increases, reheat cycles are required to achieve the required shape and the thermal exposure is increased. In addition, increasing thickness retards the heating/cooling rates. As a result, the potential for sensitization is greater in applications that require heavy wall thicknesses. The effect of the head forming operation on cladding metal properties will depend on the stage of development of the secondary phases. In many cases, some degree of precipitation can be tolerated and still provide acceptable properties. For many of these alloys, it is nearly impossible in practice to produce hot formed heads that are totally free from precipitation, and the formation of at least small amounts of one or more of these phases should be considered typical.[9]

Standardized corrosion tests have been developed to detect susceptibility to intergranular attack and localized corrosion. ASTM A262, G48, and G28 are the most common test methods for evaluating these grades. Standardized tests may not correlate with service conditions and each test has limited applicability.[11-13] Because of the complexity of applications and large number of grades, the cladding metal manufacturer should be consulted before qualifying material for specific applications. It may be appropriate to perform corrosion testing that is representative of the intended service environment and includes subjecting the test material to thermal simulation of the head forming process.

Many of the austenitic stainless steels and nickel alloys have reaction kinetics that are slow enough to permit hot forming and post forming heat treatments that are ideal for the carbon or alloy steel base metal. These cladding metals include the standard low

carbon and stabilized stainless steels, 3xxL, 321 and 347 and the more stable nickel alloys such as Alloy 625. A Time-Temperature-Sensitization diagram that demonstrates the effect of carbon in 304 stainless steel is shown if Figure 1.[14] This indicates that with 0.030 max carbon, grade 304L will have extended time when formed at 900°C and up to ~8 hrs at 600°C without sensitization.

FIGURE 1: TIME-TEMPERATURE-SENSITIZATION (TTS) OF 304 STAINLESS STEEL, EFFECT OF CARBON [14]



For these clad materials, hot forming is usually carried out at the base metal normalizing temperature. Cold or warm forming is also routinely performed, followed by stress relief heat treatment as required by UCS-79. It is also common, especially for alloy steels, to perform normalization, normalize & temper, or quench & temper heat treatments after the completion of forming operations. Such post forming heat treatment ensures that the specified base metal mechanical properties are achieved. A large number of explosion welded clad heads are in service today that were manufactured following these procedures. In many cases testing in accordance with ASTM A262 has been performed to demonstrate the finished head is not susceptible to intergranular attack.

CASE HISTORY

ASME 2:1 Elliptical Head

Head ID: 1930mm (76.00''), Clad Inside

Clad: SA240-317L, Nominal Thickness: 4.8mm (0.188'')

Base: SA516-70, Nominal Thickness: 19mm (0.750'')

Test coupon cut from explosion welded production material and heat treated to simulate head forming: 913°C (1,675°F) hold 70 minutes minimum, Air Cool.

Corrosion testing was performed in accordance with ASTM A-262 Practice 'A'. The etched structure was classified as "Dual Structure" (Figure 2) and accepted in accordance with ASTM A-262 Table 3.

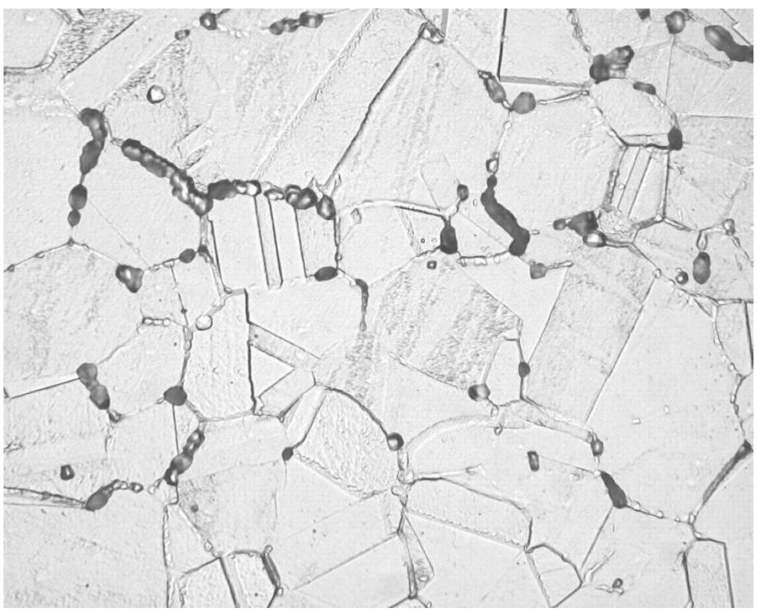


FIGURE 2: ASTM A-262 PRACRICE A, "DUAL STRUCTURE"

Other cladding metals in this group, especially those containing high Cr and Mo content, exhibit rapid reaction kinetics as is shown in Figure 3 below.[15] In these cases, the head forming options are limited and care must be taken to ensure that neither the cladding metal corrosion resistance nor the base metal mechanical properties are compromised. For cladding metals with limited thermal stability, alloy steel base metals that require post forming heat treatments to achieve mechanical properties are not an option. Whenever possible, warm or cold forming below the precipitation temperature for the detrimental secondary phases is recommended and is it essential for alloys such as C276. Stress relief in accordance with UCS-79 may still be required, but the heat treatment time and temperature must avoid sensitization.

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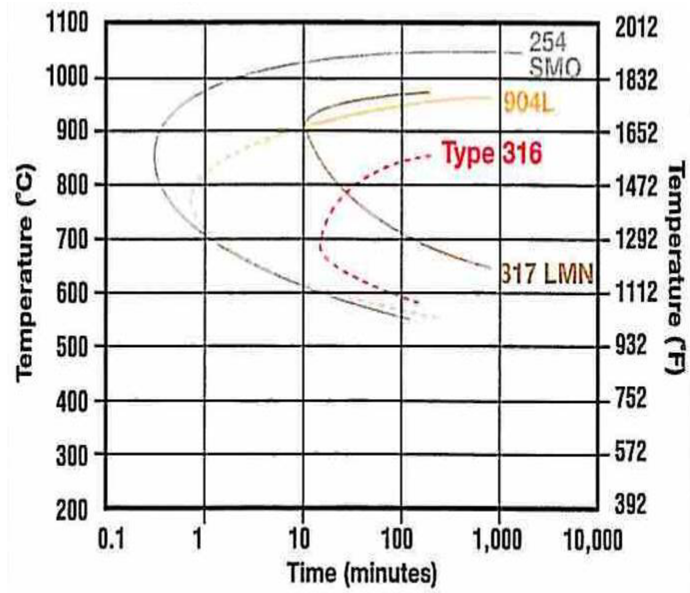
FIGURE 3: TIME-TEMPERATURE-SENSITIZATION DIAGRAM [15]



Clad heads, with base metal thickness that require forming at elevated temperatures, have been formed successfully above the upper limit of secondary phase stability at ~1050°C with cladding alloys such as C22 which exhibit intermediate reaction kinetics. Forming at this high temperature will limit precipitation of secondary phases in the cladding metal, but is not ideal for the carbon steel base metals. The normalizing or austenitizing temperature is typically just above the upper critical, A3 in Figure 4. ASME SA-516 requires an austenite grain size of 5 or finer. A fine austenite grain size improves toughness due in part to a finer distribution of the pearlite and ferrite upon cooling. As the temperature is raised above the upper critical, the austenite grain size coarsens. Slow cooling from austenitizing temperatures well above the upper critical may give rise to a Widmanstätten type structure that has limited ductility and toughness. For these reasons, it is critical that the base metal mechanical properties be qualified prior to head forming. The specific heat of material should be subjected to heat treatments that simulated the head forming operations and any required SPWHT, followed by tensile and charpy impact testing.

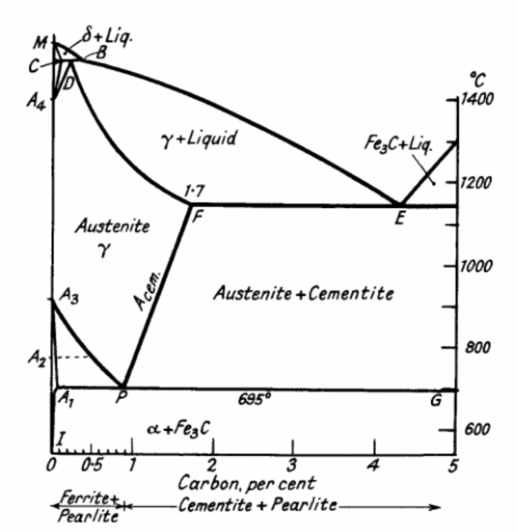


FIGURE 4: IRON-CARBON PHASE DIAGRAM

CASE HISTORY

ASME 2:1 Elliptical Head ASME 2:1 Elliptical Head

Head ID: 1391mm (54.75''), Clad Inside

Clad: SB575-C2000, Nominal Thickness: 6.4mm (0.250'')

Base: SA516-70, Nominal Thickness: 44.5mm (1.750'')

Test coupon cut from explosion welded production material and heat treated to simulate head forming: 1038°C (1,900°F) hold 180 minutes minimum, Fan Cool.

Transverse Tensile Test:

Yield Strength (Mpa)	Tensile Strength (Mpa)	% EL in 50 mm	% R.A.
333	516	30.0	68.8

ASTM Grain Size: 7

LCVN Impact Testing: Test Temperature: -40°C

Impact Energy (J): 87, 83, 117

Corrosion testing was performed in accordance with ASTM G28 Practice A & B. A second test coupon was heat treated at 900°C, 60 min, air cool, to simulate possible post forming normalization. Mechanical properties were acceptable in the as-formed condition, and the post forming normalization was not required.

Simulated HT	Practice A, Rate (mils/yr)	Practice B, Rate (mils/yr)
1038°C, 180 min	19.8	3.85
+ 900°C, 60 min	32.5	800.63

410S AND DUPLEX STAINLESS STEEL CLAD

The primary 400 series stainless steel cladding metal for which there has been significant head forming application is 410S. Clad materials with both carbon and alloy steel base metals have been successfully formed using forming procedures similar to those used for the low carbon and stabilized austenitic grades. The significant difference is that while the austenitic grades possess good low temperature toughness, 410S does not. The key is to ensure that all significant bending and deformation is performed above the ductile-to-brittle-transition-temperature for the 410S. For this reason 410S clad heads are always preheated above ambient temperatures, and most heads have been warm or hot formed at elevated temperatures.

The duplex stainless steels derive their beneficial properties from their balanced ferrite and austenite microstructure. In addition to the potential formation of detrimental secondary phases, the duplex alloys may also be damaged by upsetting this balanced microstructure. Improper elevated temperature forming or heat treatment can damage both the mechanical properties and the corrosion resistance. If the material becomes sensitized during forming, the only way to recover the properties is with a re-solution anneal heat treatment. Such heat treatment is generally not compatible with carbon steel base metals. Deleterious phases can begin to form in the duplex alloys at temperatures as low as 300°C.[16] As a result, duplex alloy-steel clad heads are generally formed below 300°C and must not be subjected to any post forming heat treatments.

TITANIUM AND ZIRCONIUM CLAD

NobelClad has extensive experience supplying formed pressure vessel heads manufactured from explosion welded reactive metal clad materials. Cladding metals include titanium grades 1, 11, 17 and zirconium 700 (low oxygen 702). The base metal has generally been SA-516 carbon steels, but there have also been applications where austenitic stainless steel base materials have been employed. In comparison with the stainless and nickel cladding alloys, the reactive metals used for explosion welding have only minor alloying and are not prone to formation of secondary phases and associated sensitization.

However, the inherent differences in structure and mechanical properties between the reactive metals and the base metals leads to reduced formability when compared with stainless steel and nickel alloy clad. The reactive metal grades employed in explosion welding are produced with low yield strength (138 Mpa). During cold forming, the low yield strength of the cladding metal can result in localized forging that may cause nonbond. As a result, cold forming of titanium and zirconium clad materials should be limited to simple shapes and relatively low forming loads.

In addition, titanium and zirconium clad interface characteristics can be significantly altered during elevated temperature processing. The iron-titanium and iron-zirconium phase diagrams show the formation of several intermetallic compounds. Although several studies have shown that intermetallic formation is limited in the as-explosion-welded condition, the bond strength can be degraded if the clad material is overheated. Time-Temperature studies have been conducted to characterize titanium and zirconium clad materials. Figure 6 shows the effect of time-temperature exposure on the shear strength of titanium clad steel. [17] This study concluded that the optimum window for successful fabrication is between 600°C – 800°C, and that exposure to temperatures above 800oC will rapidly degrade properties and should be limited. In practice, titanium and zirconium heads have been formed below 700°C to keep the carbon steel base metal below the lower critical temperature.

CASE HISTORY

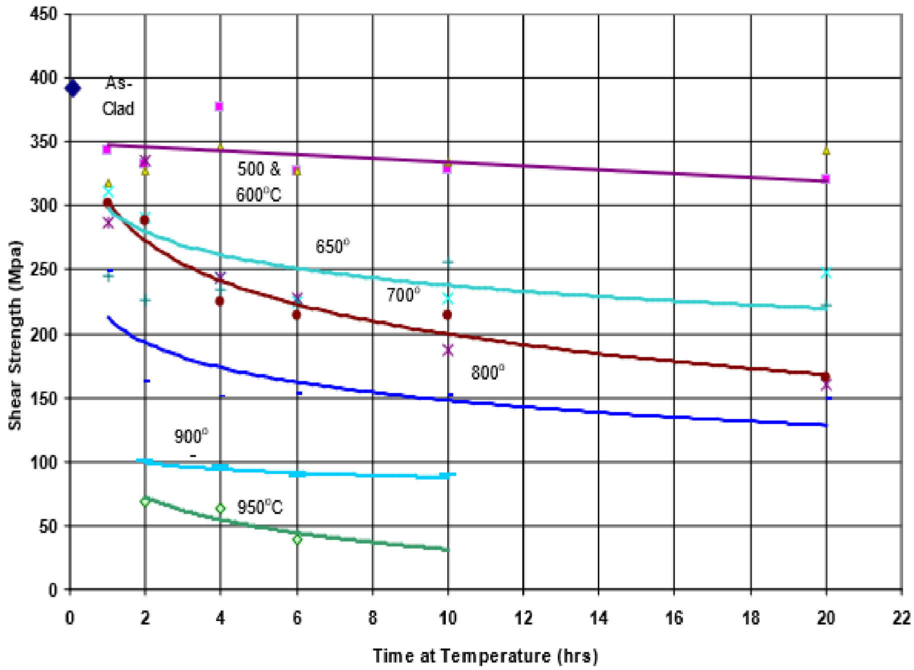


FIGURE 6: SHEAR STRENGTH OF TITANIUM-STEEL CLAD VS. TIME AT TEMPERATURE [17]

Four (4) ASME Hemispherical Heads

Head ID: 1686mm (66.4''), Clad Inside

Single Piece Construction

Clad: SB265 Gr11, 4.8mm (0.188'')

Base: SA516-70, 68mm (2.69'')

Forming Operation: Press Formed at ~675°C

Post forming UT inspection in accordance with ASME SA578, revealed no clad separation or any recordable indications. Shear strength > 140 Mpa.

CASE HISTORY

Six (6) ASME 2:1 Elliptical Head

Head ID: 4300mm (169''), Clad Inside

Segmental Construction – Crown + 8 Petals

Clad: SB265 Gr17, 9mm (0.354'')

Base: SA516-70, 100mm (4.0'')

Forming Operation: Press Formed at ~650°C

Post forming UT inspection in accordance with ASME SA578, revealed no clad separation or any recordable indications. Shear strength > 140 Mpa.

Localized cold pressing to final shape resulted in "squish" of titanium cladding metal and minor nonbond on the corner of two (2) petals.

TANTALUM CLAD

Tantalum is characterized by a high melting point, outstanding corrosion resistance in many environments, excellent ductility and a low work hardening rate. Tantalum also reacts readily with oxygen and cannot be processed in air at temperatures above 260°C (500°F). Tantalum is also very expensive, and hence the tantalum cladding metal thickness is generally only 1mm or less. The low work hardening rate and good ductility of Ta, coupled with the thin gauge of cladding metal, together with the restriction that Ta clad must be formed cold, results in a clad material that is susceptible to mechanical damage and is difficult to form. Production tantalum clad

heads have been manufactured successfully by employing segmental construction, special tooling, and low temperature preheats.[18]

CONCLUSIONS

Improper forming conditions can result in loss of cladding metal corrosion properties, inappropriate base metal mechanical properties, and/or clad separation. Important metallurgical consideration in head forming of common cladding materials are summarized below:

- Stainless steel and nickel alloy clad may be formed over the entire forming temperature range without risk of clad separation. Consideration must be given to the requirements of UCS-79 when heads are cold formed.

- The stabilized stainless steels and stable nickel alloys may be hot formed successfully without unacceptable levels of sensitization.

- Many of the stainless steels and nickel alloys exhibit rapid formation of secondary phases, and consequently, the head forming procedure must take reaction kinetics into account to ensure that anticipated corrosion resistance is obtained.

- Forming of some thick, nickel alloy clad may require hot forming above the upper limit of secondary phase stability to avoid sensitization. In these applications, it is critical that qualification of the steel base metal include simulation of forming operation to ensure mechanical property compliance.

- For titanium and zirconium clad materials, cold forming should be limited to simple shapes and low forming loads. The optimum temperature range for forming of reactive metal clad is 600-700°C.

NobelClad has extensive experience with the conventional clad metal combinations and has established forming parameters which result in reliable corrosion resistance of the cladding metal, Code compliant base metal, and absence of interface problems.

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