DRILL STEM STEELS FOR USE IN GEOTHERMAL ENVIRONMENTS*

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ABSTRACT

Steels which are used in drill stem for conventional drilling have been selected primarily to satisfy certain static strength requirements and cost considerations. As the environments in which drilling is performed become more severe (e.g. in geothermal fluids) additional considerations must be given to the design of alloys which are resistant to general corrosion, stress corrosion, and corrosion fatigue. General design considerations for steel alloys which should provide an enhanced resistance to geothermal drilling operations are presented. These considerations include discussion of the chemistry and metallurgical substructure, and how their variation affects the mechanical and corrosion properties of steel used for drill stem applications. A duplex ferritic-martensitic steel has an advantageous combination of compositional and microstructural features which should lead to improved chemical resistance (particularly to hydrogen sulfide) as well as provide a good combination of strength and toughness properties. This duplex steel is based on the iron-2.0 weight percent silicon-0.1 weight percent carbon system, and offers the potential of enhanced performance in geothermal drilling as well as low alloy cost.

INTRODUCTION

Energy recovered from geothermal resources can be converted into a usable form, but the economics of this conversion will, of course, govern the development of this energy source. A large portion of the cost of geothermal energy development arises from the expense of the drilling operation. Of particular concern is the cost of materials involved in the drilling (e.g. drill stem, drill bits, etc.) and the additional cost incurred due to the failure of certain components. A notable illustration of a particularly devastating failure is the downhole fracture of the drill stem, leading to expensive "fishing" operations.

Current drilling practice in geothermal environments often uses materials which meet certain American Petroleum Institute (API) requirements [1]. These requirements were originally drafted for the bulk of oil and gas well drilling where the environments encountered are usually quite benign or when aggressive corrosives are encountered, modifications in mud chemistry can control the attack to manageable proportions. The downhole environment in geothermal drilling is often very hostile; also the drilling must proceed through entirely different geologic formations, such as fractured zones, where mud drilling is not appropriate. In that case, air drilling is used where air is the fluid used to carry the cuttings. In air drilling the large amount of oxygen present in the environment surrounding the drill stem can greatly increase the corrosive attack on the steel. The addition of chemicals to the air stream to inhibit corrosion is certainly more difficult to administer and control

than in mud drilling. Corrosion of the drill stem in geothermal drilling is thus a serious problem. This article addresses the problem through a discussion of the metallurgy of the steels used for drill stem applications. The general comments on the relationship between microstructure and alloy chemistry on the mechanical and corrosion properties of steel can, in many respects, also be applied to other geothermal applications (e.g. well casing).

CORROSION IN GEOTHERMAL ENVIRONMENTS

The fluids (including gases) encountered in geothermal drilling are complex, variable mixtures whose characterization is difficult [2,3]. The chemical composition of specific geothermal fluids can be identified, but it varies greatly from site to site. These fluids in general contain several chemical species which can produce significant corrosion of ferrous materials [4]. These chemical species include: hydrogen sulfide, hydrogen (ion or atom), chloride ion, carbon dioxide, and ammonia. The reactivity of each of these chemical species varies with concentration and with the concentration of the other species present. The interaction of two or more chemical species may give results which are greatly different from those obtained with the individual species alone. Other chemical species may be present in geothermal fluids which are less common or aggressive, but can also induce corrosion. Examples include sulfate ion, fluoride ion, heavy metals, and boron. Temperature may also play a critical role, and in geothermal drilling may range from ambient (topside) to generally less than 530 K (this may possibly run to as high as 650 K in extreme cases). Because of fluid circulation, the drill stem will see a lower temperature than the downhole maximum.

Oxygen is generally not a naturally occurring component in geothermal fluids, but if externally introduced into the system may greatly increase corrosion. The oxygen which is brought in through air drilling operations is a particularly important cause of the high corrosion rate in drill stem. The

general (uniform) corrosion rate of low alloy steels is increased as the oxygen concentration and temperature are increased. The iron oxide scale is often not very adherent; further, this scale can be abraded away by cuttings being carried up the pipe. Thus, the surface oxide layer may not remain intact and, therefore, will provide little aid in preventing further corrosion. The presence of oxygen also allows other types of corrosion to become active; it is particularly important in promoting sulfide stress cracking and stress corrosion cracking.

The general corrosion rate of low alloy steels increases rapidly with decreasing pH (e.g. increasing hydrogen ion content), especially below pH7. Geothermal fluids usually fall in the 3 to 9 pH range. The passivity of many low alloy steels is pH dependent. Changes in pH can cause breakdown of passive films in local areas, and this can lead to serious localized attacks such as pitting, crevice corrosion, and stress corrosion cracking.

Chloride ions are found in a wide range of concentrations in geothermal fluids; the range can vary from 1,000 to 120,000 ppm or more. Chloride ions are primarily damaging in that they can also cause the localized breakdown of passive films, and again the resulting localized attack can take place in the form of pitting, crevice corrosion, or stress corrosion cracking. Hydrogen sulfide (in the range of 0.1 to 300 ppm in geothermal wells) is another species which can cause severe localized attacks in steels. High strength steels are particularly susceptible to sulfide stress cracking. Carbon dioxide (found in concentrations of 60 to

1,000 ppm) and ammonia (0.2 to 300 ppm) in general accelerate the uniform corrosion rates in low alloy steels.

Although uniform corrosion is certainly objectionable, its behavior is fairly well understood [4], and its major effects involve an overall loss of wall thickness and thus a decrease in strength-related properties. In contrast, the mechanisms of localized attack are less generally understood [4] or predictable. More importantly localized attack can cause failure within a short period of time. Because of the costly effects of unpredictable failure, elimination of localized attack is the most important objective in controlling corrosion of drill stem. It is, of course, also desirable to limit the uniform corrosion; however, it can at least be monitored and its damage assessed and compensated for. The drill stem can then be replaced as necessary before catastrophic downhole failures can occur; thus preventing costly fishing operations.

From cost considerations, drill stem steels generally have a low alloy content and have a ferritic/martensitic (body centered cubic or tetragonal) phase structure. These types of steels are in general susceptible to sulfide stress cracking (e.g. due to hydrogen embrittlement); they are much more susceptible than austenitic (face centered cubic) steels. Low nickel or nickel free ferritic/martensitic steels are, however, much more resistant to cracking from chloride ions than many austenitic stainless steels which suffer from extreme susceptibility to this form of stress corrosion cracking. Since drill stem is made from ferritic/martensitic steels, greatest consideration will be given to the question of

how the resistance to hydrogen embrittlement (of which sulfide stress cracking is one form) may be improved. Chloride cracking is not a major problem in ferritic/martensitic steels and will not be considered further. The effects of uniform corrosion and how corrosion resistance may be enhanced in steels will also be considered.

CURRENT REQUIREMENTS

The current API requirements [1] for selection of drill stem steel are based solely on keeping the yield and tensile strengths within a certain range (see Table 1 for specific grades). The composition specifications contain maximum acceptable limits on only sulfur and phosphorus (0.060 and 0.040 weight percent respectively). No other composition specifications are given. Due to the broad manner in which the requirements are written, a wide range of steel compositions and heat treatments can properly be supplied by the various drill stem manufacturers. A range of alloy compositions and heat treatments can lead to some possible significant variations (within a single drill stem grade) in mechanical properties (toughness, fatigue, etc.) and chemical resistance (corrosion and hydrogen embrittlement resistance) as well as behavior controlled by a combination of both properties (in particular corrosion fatigue). However, even if the drill stem from various suppliers were fairly uniform in composition, it is quite apparent that the chemistry of these steels has not been adjusted to maximize resistance to the hydrogen sulfide containing environment often confronted in geothermal drilling.

The steels which are generally used for drilling in hydrogen sulfide containing environments are low-alloy, medium-carbon steels (usually API Grade E). The main alloying constituents are "normally": carbon (0.38 to 0.45 weight percent), manganese (1.35 to 1.65 weight percent), and molybdenum (0.10 to 0.15

weight percent). The silicon level is generally about 0.25 weight percent and the sulfur and phosphorus are held below the limits specified by API of 0.060 and 0.040 weight percent respectively. Small additions of vanadium or chromium (generally less than 0.10 weight percent) may also be added depending on the normal practice of the manufacturer. The drill stem is generally supplied in either the quenched and tempered, or normalized and tempered heat treat condition (steel heat treatment will be discussed in a subsequent section).

It should be noted that the composition supplied for Grade E drill stem may vary significantly from that which is listed above as "normal". For example, steel which has been downgraded because it fails to make the strength requirements for a higher grade (x-95 for example) could be supplied (according to specifications) as a lower grade (Grade E) pipe. The additional strength and hardness above that normally found in Grade E can cause catastrophic problems in hydrogen sulfide containing environments.

A substantial amount of research has been performed with the aim of establishing guidelines for selection of materials for use in hydrogen sulfide containing oil field environments (see for example references 5-14). Many of the conclusions drawn from these studies are also applicable to geothermal drilling. Three general conclusions pertinent to drill stem which have been drawn from these studies are:

1. for ferritic/martensitic steels heat treated to hardness less than R_{c22} (ultimate tensile strength equal to about 794 MPa or 115 ksi), sulfide stress cracking is not a serious problem

2. for a given type of heat treatment, (i.e., normalized or quenched and tempered) susceptibility to sulfide stress cracking increases with increasing hardness (strength)
3. for a given hardness (strength) level, susceptibility to sulfide stress cracking varies with heat treatment and/or the resulting microstructural changes.

Based on a compilation of research on stress corrosion, the National Association of Corrosion Engineers (NACE) has proposed NACE Standard MR-01-75, Material Requirements for Sulfide Stress Cracking Resistant Metallic Materials for Oil Field Equipment.

The portion of this standard relating to steel drill stem specified that normalized steels with a hardness of greater than $R_c 22$ not be used in sour well environments. In the event that higher strengths are required, the NACE Standard allows the use of certain specified (low nickel) steels in the quenched and tempered condition up to hardness of $R_c 26$ (ultimate tensile strength of about 876 MPa or 127 ksi).

The NACE Standard makes an important contribution to the method of selecting materials for use in hydrogen sulfide containing environments. This standard bases its selection requirements on (static) stress corrosion cracking tests; this may not be fully adequate considering the cyclic nature of the load on the drill stem during the drilling operation. It is generally appreciated that an alternating loading can cause fatigue failures in metal components at stress intensity levels well below those required to cause yield or rupture when applied continuously [15]. Fatigue failure of steel drill stem is a problem that has been known in the drilling industry for

decades [16]. When pipe is rotated through a curved portion of the hole (a dogleg) the loading on the pipe undergoes a cyclic variation, that is, fatigue stresses are induced. The fatigue stress is itself often large enough to cause failure of the drill stem after a number of cycles, but the fatigue problem is most severe when drilling takes place in a well containing hydrogen sulfide. This is consistent with the results shown in a number of metal/environment systems; the combined effects of environmental attack and fatigue are more severe than would be predicted from their separate effects [17]. It has been found that failures can often be prevented in (static) stress corrosion tests by lowering the stress below a critical intensity level, however, no such level has been found to prevent failure when a cyclic stress is applied. Thus, materials selections based on static stress corrosion tests may not go far enough to assure the absence of failures initiated by cracking in hydrogen sulfide containing environments. Future standards should consider the susceptibility of drill stem to hydrogen sulfide under fatigue conditions in addition to static stress conditions to determine the suitability of particular steels to drilling in geothermal environments.

Previous work [17,18] has shown that the heat treatment of steels (specifically, normalized versus quenched and tempered structures) seems to have little if any effect on corrosion fatigue properties; this is in direct contrast with results found from (static) stress corrosion tests. Further, studies [17,19]

have demonstrated that changes in the chemistry of steels have an effect on corrosion fatigue only if the change affects the corrosion (including hydrogen) resistance. Thus, to improve the corrosion fatigue properties, a change in steel chemistry would probably be effective only if it improves the resistance to the corrosive under no load. Various aspects of steel composition and microstructure which are instrumental in determining the chemical resistance and mechanical properties important for drill stem steels are discussed in the next sections.

ALLOYING EFFECTS IN STEELS

The role of various alloying elements in ferritic/martensitic steels are discussed below from the point of view of their effect on various mechanical and chemical properties [4,20,21]. The principal alloying elements likely to be found in drill stem steels are carbon, manganese, silicon, and molybdenum. Other (generally more expensive) alloying agents can also be employed. These may include elements such as chromium, vanadium, niobium, and nickel. Sulfur and phosphorus are also present in steels, usually as undesirable residuals. Since the corrosive species of primary interest in geothermal environments is hydrogen sulfide, the effect of the variation of these elements with respect to hydrogen embrittlement will be emphasized (sulfidation may become important at substantially higher temperatures).

The sulfur and phosphorus which are present in steel used for drill stem are undesirable since they invariably reduce the toughness. Phosphorus is present in solution in ferritic/martensitic alloys, and it undoubtedly concentrates at grain boundaries. While phosphorus increases the strength and hardness of steel, it also tends to greatly decrease ductility and impact strength, particularly for steel in the quenched and tempered condition. Temper embrittlement has also been shown [22] to be increased with an increase in phosphorus content in alloy steels.

Sulfur is also considered to be an undesirable tramp element in that it acts to decrease transverse ductility and impact strength. Sulfur (occurring without manganese) forms a

continuous grain boundary film of iron sulfide which has a low melting point and is brittle; this leads to embrittlement problems during hot working or heat treating. However, when manganese is present, the sulfur is formed into inclusions of manganese sulfide which are easily deformed (elongated) during hot working processes. The resultant elongated inclusions adversely affect toughness and bend formation. An increased sulfur content also leads to a decrease in general corrosion resistance (pitting at manganese-sulfide or iron-sulfide inclusions which intersect the surface is common).

Both sulfur and phosphorus are also deleterious to the behavior of steels in hydrogen-containing atmospheres. Their detrimental effect in hydrogen can be related to the close connection between hydrogen embrittlement and temper embrittlement [23,24]. Since sulfur and phosphorus are undesirable to both the mechanical properties and chemical resistance (particularly to hydrogen embrittlement) of steels, it would be beneficial to keep these residuals to as low a level as possible during the manufacture of drill stem steel. Any sulfur that does, however, remain in the steel should be controlled by rare earth additions [25] rather than manganese additions. The rare earths combine with the sulfur to form rare earth sulfide inclusions which are better able to withstand elongation during hot working. Such "shape controlled" sulfides contribute to a marked improvement in toughness and formability of the steel and also present considerably less inclusion interface area (which promotes hydrogen embrittlement).

Carbon is used in steels as the principal hardening and strengthening agent. Carbon is, in fact, the element in steels which allows them to attain such unique and useful microstructures. Iron-carbon alloys can be heat treated (e.g. austenitized, quenched, tempered, etc.) to yield combinations of phases and grain size from which the final mechanical properties of the alloy can be regulated. The carbon content and its disposition in the matrix must, however, be controlled in order that ductility and toughness are maintained at reasonably high levels. Increasing levels of carbon in ferritic and martensitic steels have been found [21] to increase the susceptibility of steels (at constant strength levels) to hydrogen embrittlement. In relatively low-strength steels, an increasing carbon content also increases the extent of hydrogen cracking as the strength level increases. Carbon appears to have much less of an effect on the general (uniform) corrosion rate of steels, however the prevailing trend is for increasing carbon to increase the corrosion rate. Considering both toughness and chemical resistance, the reduction of the carbon level in drill stem steel would seem to be desirable if this can be done while still maintaining the necessary strength level.

Manganese is present in steels for two main reasons: firstly, it acts as a hardening and strengthening agent (it increases the hardenability, which is the ability to transform to martensite at reduced cooling rates), and secondly, it acts as a deoxidizer and sulfide former. These latter "chemical" functions tend to improve the alloy's surface properties as

well as increase toughness and reduce "hot shortness" problems. Increasing the manganese content above about 2% (by weight), however, adversely affects the toughness and ductility of many steels. Minor variation of manganese in plain carbon steel has little effect on the uniform corrosion rate in most corrosives, but manganese appears to be even more detrimental than carbon in increasing the susceptibility of ferritic and martensitic alloys to hydrogen embrittlement. Studies [26,27] show that the stress necessary to induce cracking decreases with increasing manganese levels. The mechanism accounting for this increase has not been fully identified; one model suggests that the presence of manganese may cause the crack tip to become more cathodic (thereby increasing the affinity for hydrogen). It has also been suggested that manganese might also increase the dissociation rate for molecular hydrogen thereby increasing the amount of atomic or ionic hydrogen which can penetrate into the lattice.

Manganese is used commonly as an alloying addition because it is a cheap and straight forward means of strengthening ferrite, and it permits low-alloy steels to be used at higher strength levels. However, when considered in terms of compatibility with hydrogen-containing environments, alloying with manganese appears to be a poor choice. Manganese is very effective in terms of strengthening, sulfide formation, and deoxidation, but these effects can be fulfilled by other alloying additions [20]. As was mentioned previously, the sulfide formation can be accomplished more suitably (e.g. formation of more chemically

and physically stable inclusions) by rare earth additions. Deoxidation can be accomplished by aluminum, silicon, or rare earths. Finally, other elements can be added so that the hardenability requirements will be met; this will presently be discussed.

Silicon is the principal deoxidizing element added to steels. Silicon is also a very effective solid solution strengthener and hardenability enhancer; it is in fact superior to manganese in these functions. Silicon is kept below certain levels (generally about 0.35 weight percent) primarily because higher levels often increase the ductile-brittle transition temperature in quenched and tempered structures. Silicon can improve the general corrosion resistance of steels if it is kept from promoting the formation of inclusions. High levels of silicon (2 weight percent or greater) are capable of imparting increased resistance to chloride stress corrosion cracking and help in resisting pitting and intergranular corrosion. Silicon also appears to be quite beneficial in promoting resistance to hydrogen embrittlement; this is the case for both high- and low-strength ferritic/martensitic steels [28,29,30]. No consensus on the mechanism which causes this improvement emerges from the literature, but is it likely that it is caused either from the increase in carbide stability due to the silicon, or by the effect of silicon on the hydrogen diffusivity in iron. Although its role may be complex, the ability of silicon to promote resistance to hydrogen embrittlement, and corrosion in general, strengthen ferrite

and increase hardenability, makes it an attractive alloying element for steels which are used for drill stem applications, if the toughness can be maintained at an appropriate level.

Other alloying elements (namely nickel, molybdenum, chromium, vanadium) can be added to improve the mechanical properties of ferritic and martensitic steels. However studies [31] involving the additions of these elements have raised contradictory claims concerning their effect on hydrogen embrittlement. The addition of minor amounts of carbide formers (molybdenum, vanadium, chromium) may be somewhat beneficial in improving hydrogen embrittlement resistance by stabilizing carbides. The available studies however, indicate that under most conditions, minor adjustments in these elements (keeping them less than one weight percent) do not have a large effect on hydrogen resistance. Similarly, small alloying additions also have very little consequence on the overall corrosion resistance of steel. Since the addition of these elements is expensive, it is most desirable to arrive at an alloy which minimizes their use.

Nickel is an extremely common alloying element which is added to steels. It can (if added in sufficient quantity) improve toughness and corrosion resistance, as well as improve the heat treat response of the steel. The addition of nickel has, however, been associated with greatly increasing the susceptibility to stress corrosion cracking (particularly in chloride-containing environments). The NACE Standard MR-01-75 ('78 revision) requires

that steels contain less than one weight percent nickel. Because of the NACE requirement, and the cost of nickel, steels designed for geothermal drilling should have no, or at most, a very limited amount of nickel.

Additional elements not commonly used in iron alloys may prove useful in improving hydrogen resistance. One such element is titanium. Titanium has a strong chemical affinity for hydrogen and seems to act as a "hydrogen trap." The experimental verification for this effect and for the influence of titanium on mechanical properties is only in the early stages of investigation [32]. The possibility of additions of titanium or another similarly acting elements is an area which could prove to be beneficial for improving the resistance of drill stem alloys to hydrogen sulfide.

MICROSTRUCTURAL EFFECTS

Solute additions to steels can directly affect hydrogen embrittlement either adversely or positively by a chemical interaction with hydrogen, or indirectly through their role in controlling crystal structure, grain size, and texture. Although the direct effect of alloying additions certainly can not be entirely separated from microstructural changes, the effect of various changes in the microstructure on mechanical and chemical properties will be discussed as though they are independent variables.

Grain size is an important variable which affects alloy properties. It appears that all mechanical properties important to alloy usage (at all but very high temperatures) can be improved by refinement of grain size and substructure. A fine grain size not only improves strength and toughness, but also enhances resistance to hydrogen embrittlement. Research [33] indicates that a refined grain size increases the resistance to hydrogen by increasing the number of trapping sites.

A strong texture in steel alloys increases the directionality of mechanical properties. Highly textured steel is stronger in specific directions than in others; ductility and toughness are also strongly direction dependent. Similarly, the resistance to hydrogen cracking is directionally dependent [34], but since the manufacturing methods for producing seamless drill stem also produce a texture which is difficult (and uneconomical) to change; the alteration of texture will not be further considered.

In ferritic and martensitic steels, there appears to be a strong relationship between the crystal structure and the susceptibility to environmental embrittlement (under a static stress) [7,8]. Untempered martensite is the most deleterious structure for use in a hydrogen-containing atmosphere. This is associated with the presence of brittle martensite and the high level of residual stress; these are the same factors which dominate the mechanical properties, and make the untempered martensite strong and hard but not tough. The most preferred substructure (for conventionally heat-treated ferrous alloys) is one which combines a well-tempered martensite or bainite with a refined plate (or lath) size and a uniform dispersion of carbides. This seems to yield the best resistance to hydrogen-embrittlement as well as producing an alloy which has a good combination of strength and toughness. Other conventional microstructural conditions such as normalized or quenched and partially tempered crystal structures generally have properties which fall between the limits of the structures discussed above. Specifically, the resistance to hydrogen embrittlement, strength and toughness (fatigue resistance, etc) lie in an intermediate region. For the case of a fatigue-type load in a corrosive environment, it is less certain that the phase structures, which are commonly obtained, play a dominant or clear-cut role [17].

GENERAL PROPERTY-DESIGN CONSIDERATIONS

An important conclusion from the preceding discussion on alloy composition and microstructural effects is that certain trade-offs must be made in the design of steels for specific uses. In the case of steel for drill stem applications, the steel must attain a certain strength level and fatigue resistance, and also retain a good toughness. When used in certain drilling applications (specifically geothermal drilling) the steel should also show a suitable resistance to certain kinds of corrosion and corrosion fatigue. Resistance to hydrogen sulfide which can often cause sudden and catastrophic drill stem failures is particularly important. The mechanical and chemical requirements must also be balanced with economic requirements which limit the use of expensive high alloy steels.

The general variations in important parameters controlling strength, toughness, and hydrogen embrittlement will be briefly summarized below, and will then be related to obtaining a steel most suitable for drilling in geothermal environments.

High strength can be obtained by:

1. solid solution strengthening (e.g. carbon in iron)
2. precipitation strengthening (e.g. alloy carbide formation)
3. solid state phase transformation (e.g. martensite in steels)
4. refinement of grain size and substructure
5. hot and cold working (including thermomechanical processes)
6. dispersion strengthening (e.g. oxide particles in nickel alloys)

Toughness and ductility are generally increased by:

1. refinement of grain size and substructure,
2. controlling the shape and distribution of precipitates and inclusions,
3. eliminating (or modifying) the formation of brittle phases,
4. employing ductile phases as crack arrestors.

Resistance to hydrogen embrittlement can be enhanced (in ferritic/martensite steels) by:

1. use of solutes which suppress local hydrogen reactions at crack tips or at specific precipitates (e.g. silicon in steel) and reduction of solutes which increase these local reactions (such as manganese and carbon),
2. refinement of grain size and substructure,
3. reducing planar slip by increasing the stability of coherent precipitates (e.g. silicon stabilizes carbides),
4. addition of solutes which trap hydrogen (e.g. titanium in steel),
5. reducing inclusion interfacial area (e.g. reduce total sulfur content and form rare earth sulfides).

The above lists when combined, indicate that certain courses may be followed in trying to improve the properties of drill stem steels for use in geothermal environments. Concerning the steel composition, manganese and carbon should be reduced and silicon increased as much as possible, compatible with the strength and toughness requirements. Tramp elements such as sulfur and phosphorus should be reduced to as low a level as possible. Further, certain sulfide inclusions (specifically manganese sulfide) should be eliminated; sulfur control and sulfide shape stabilization can be accomplished by rare earth

additions. The grain size and substructure should be reduced to as fine a scale as possible. Carbides should be stabilized (thermally and mechanically) by use of selected carbide formers (such as vanadium). Ductile phases should be employed as crack arrestors. Secondary phases can also be employed to control hydrogen diffusion or to change the potential at the crack tip as it penetrates this second phase. Many of the above considerations for producing a hydrogen resistant steel with sufficient mechanical properties can be included in a class of steels known as duplex phase steels which will be described in the following section.

STEELS FOR DRILL STEM APPLICATIONS

The steels which are commonly used for drill stem are usually quenched and tempered or normalized and tempered. These heat treatments can be summarized by referring to Figure 1a which is the iron rich corner of the iron-carbon phase diagram. When a steel is quenched and tempered, the steel is heated above the A_3 line and quickly cooled (quenched) to room temperature (or below) thereby causing the austenite (fcc crystal structure) to transform to martensite (bct crystal structure). The as-quenched martensite is a hard, brittle alloy until it is heated (and held for some period of time) at a temperature below A_1 . At this "tempering" temperature, precipitation of carbon out of the martensite occurs along with residual stress relief, these combine to yield a somewhat less hard and strong material, but with a significant increase in toughness. A schematic of the quench and temper process is shown in Figure 1b. A material that is normalized is air cooled rather than quickly quenched. It can also form a martensitic structure (or a closely related bainitic structure), or a ferrite and carbide mixture depending on the hardenability which is a function of alloy content of the steel. Tempering of a normalized steel will produce a structure which is generally some combination of tempered martensite, ferrite and spherodized carbides.

The problem of using low alloy steels in hydrogen sulfide containing atmospheres has been approached [35-41] for the most part by attempting to modify conventional quenched and

tempered steels. Steel manufacturers and oil companies have concentrated much of their work on AISI 4130 alloy steel, and have moderately raised the level of sulfide stress cracking resistance. The AISI 4130 alloy steel nominally contains 0.5 weight percent manganese, 1.0 weight percent chromium, 0.20 weight percent molybdenum and 0.30 weight percent carbon. Careful attention to compositional control, including strict limitations on inclusion level, and an increase in chromium and/or niobium have allowed an increase in the resistance to hydrogen embrittlement to be achieved. An alternate approach [41] is based on manganese-molybdenum modified steels in which the molybdenum level is raised above the levels conventionally used for drill stem (to a total of 0.75 to 1.0 weight percent). This approach offers lower alloy cost and good compositional control during the steelmaking process; well controlled heats of this steel have led to a level of resistance to hydrogen sulfide which is even higher than that found for the modified AISI 4130 steels at the same strength levels.

The approaches described above have the advantage of working with a commonly used steel; a steel for which the steel making and treating processes are well known. Because they are so familiar, their introduction as alternate drill stem material may be more readily accepted when compared with newer, less familiar steels suggested for the same uses. The modified 4130 steels still utilize the same heat treatment

(namely quench and temper) which yields a familiar tempered martensite structure. Unfortunately, the changes in composition discussed in the previous section which should lead to an improved hydrogen resistance are difficult to impose on a quenched and tempered steel which will still maintain good strength and toughness properties. Recent research [42,43] in the area of unique heat treatments of iron alloys has produced steels which incorporate a strong martensitic phase as the load carrying constituent in a ductile ferrite matrix. These steels have been called duplex ferritic-martensitic steels, or more commonly duplex steels. This heat treatment involves quenching the steel from the austenitic phase (temperature above A_3) to room temperature to form untempered martensite. Then, rather than tempering, the material is heated above A_1 (but below A_3) into the austenite and ferrite two phase region. It is held at this temperature until an equilibrium mixture of ferrite and austenite is formed. The alloy is then quenched to room temperature causing the austenite to transform to martensite within a ferrite matrix. The heat treat schematic is shown in Figure 2b for an iron-carbon-silicon alloy (note the effect of silicon on the phase diagram by comparing Figures 1a and 2a [43]). These duplex phase steels offer, in general, very good combinations of strength and ductility. One particular steel contains 2.0 weight percent silicon and 0.1 weight percent carbon (nominal composition) and has a combination of strength and ductility properties superior to plain carbon or controlled rolled high strength-low alloy steels

(such as Van 80). The combination of strength and ductility properties is also superior to the steels normally used as drill stem steels (such as Grade E). More importantly, from the previous discussion (as well as recent experimental work) [28,44] on the chemical adjustments desired for improvement of hydrogen embrittlement resistance, this steel would seem to be ideal. Both the carbon and manganese levels are lower, and the silicon content is significantly higher. Yet this is accomplished without decreasing the alloy's strength, and indeed an increase in toughness can be achieved. This type of steel thus has many desirable compositional and structural features suiting it for use in drill stem.

Further adjustments can be made to the basic chemistry and heat treatment described above to include other changes in microstructure which should improve the resistance to hydrogen. For instance, cyclic heat treatments and/or controlled working (hot and warm) can cause the grain size to be refined (both the ferrite and martensite). Additions of strong carbide-forming elements (such as vanadium) may allow the tempering of the two phase structure into a tempered ferrite and martensite with a distribution of stable alloy carbides. It has also been suggested [45] that duplex phase steels can contain very fine layers of austenite retained between the martensite laths. Such a retained austenite structure may prove beneficial in providing a diffusion barrier to hydrogen in steel. If this duplex phase steel (with appropriate modifications) is made with attention to limiting total sulfur

and phosphorus and controlling the remaining sulfur with rare earths, almost all of the suggestions offered for a hydrogen resistant steel with good strength and toughness can be included in one steel. The cost of this steel should be comparable to the cost of conventional good quality hydrogen sulfide resistant drill stem. Although the heat treatment needed to produce the duplex phase structure is more costly than that for the conventional quenched and tempered structure, this increase should be approximately offset by the reduced cost of alloying additions. Research to characterize the chemical and mechanical properties of such a modified duplex ferritic/martensitic steel is currently ongoing at Sandia Laboratories - Albuquerque.

SUMMARY

This paper has treated some of the important factors concerning the use of ferritic and martensitic steels as drill stem in geothermal environments. The geothermal environment with respect to the corrosion of steel has been discussed. The presence of hydrogen sulfide and oxygen have been singled out as creating the largest corrosion problems. The composition of low alloy steels was discussed, relating changes in composition and microstructure to the chemical and mechanical properties. Of particular interest was the effect of alloying additions and microstructural changes on the resistance of the low alloy ferritic steels to hydrogen embrittlement (sulfide stress cracking) and corrosion fatigue. Some general guidelines to be followed for producing a steel with improved hydrogen resistance without degradation of alloy strength and toughness were presented. A steel which meets these guidelines was then discussed. This steel is the result of a unique heat treatment and possesses a microstructure which should be very resistant to hydrogen embrittlement and also show an improved general corrosion resistance. Further, the alloying additions necessary for this steel are very inexpensive. Duplex steels thus seem to be good candidates for use as a drill stem steel in geothermal environments.

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TABLE 1
TENSILE REQUIREMENTS FOR DRILL STEM [1]

GRADE	YIELD STRENGTH		TENSILE STRENGTH
	Min.	Max.	Min.
D	380MPa(55 KSI)	--	656MPa(95 KSI)
E	518MPa(75 KSI)	--	690MPa(100 KSI)
X-95	656MPa(95 KSI)	863MPa(125 KSI)	725MPa(105 KSI)
G-105	725MPa(105 KSI)	932MPa(135 KSI)	794MPa(115 KSI)
S-135	932MPa(135 KSI)	1139MPa(165 KSI)	1001MPa(145 KSI)

The steel shall also have a minimum elongation (e) which exceeds

$$e = 625,000 A^{0.2}/U^{0.9}$$

where A is the cross sectional area of the tensile test specimen (in square inches) and U is the minimum tensile strength (in psi).

Figure Captions

Figure 1. Quench and temper heat treatment of an iron-carbon alloy; (a) phase diagram and (b) heat treatment schematic.

Figure 2. Duplex ferritic-martensitic heat treatment of an iron-carbon-silicon alloy; (a) phase diagram and (b) heat treatment schematic.

(a)

(b)

(a)

(b)