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WELDED JOINT CRACKING IN MARTENSITIC STAINLESS STEEL PRECIPITATION-STHREGTHENED WITH COPPER

PĘKANIE ZŁĄCZ SPAWANYCH STALI NIERDZEWNEJ MARTENZYTYCZNEJ UTWARDZANEJ WYDZIELENIOWO MIEDZIĄ

Problem of welded joint cracking in the HAZ of Cu strengthened 17-4PH grade precipitation hardening martensitic stainless steel is presented. Hypothesis concerning hydrogen embrittlement origin of the cracks is opposed. It was concluded that the cracks located in the high-temperature zone of the HAZ exhibit characteristics of hot cracks which originated as a result of steel embrittlement in the presence of Cu rich liquid phase. The mechanism of steel surface enrichment in Cu is proposed. Practical methods of cracks elimination are presented.

Keywords: 17-4PH grade, Weldability Testing, Copper, Liquid Metal Embrittlement, Stainless Steel, GTAW; Fracture

W artykule przedstawiono problem pękania w strefie wpływu ciepła stali nierdzewnej martenzytycznej utwardzanej wydzieleniowo miedzią. Podważono literaturowe informacje wskazując, że są to pęknięcia zimne spowodowane kruchością wodorową. Stwierdzono, że pęknięcia zlokalizowane w wysokotemperaturowym obszarze SWC mają charakter pęknięć gorących i powstały w wyniku kruchości stali w obecności cieczy bogatej w miedź. Wyjaśniono mechanizm wzbogacania się powierzchni stali w miedź oraz podano technologiczny sposób eliminacji pęknięć.

1. Introduction

The weldability of precipitation hardening martensitic stainless steels is recognised due to the extensive use of these steels in welded structures in a wide range of industries, and especially in the aerospace sector. The literature describes this weldability as good or very good. One often finds positive remarks regarding the low susceptibility to welded cracking. Usually, neither preheating or post-weld heating is considered necessary to obtain sound joints in thicknesses up to 100 mm (4 inches) [1, 2]. However, in spite of this broadly accepted assessment of the good weldability, manual GTAW (Gas Tungsten Arc Welding) fillet weld joints of 17-4PH steel (sheet metal and thick plate) have not been free of defects. Inspection has revealed the presence of fine surface cracks in the HAZ (Heat Affected Zone) area in certain areas of the joints. These locations were fillet weld curvatures and weld bead overlaps (Fig. 1). The 17-4PH steel used is equivalent to X5CrNiCuNb16-4 according to PN EN 10088-1 standard (polish version of European Union standard) [3]

and has the following chemical composition: <0.07% C, (15-17)% Cr, (3-5)% Ni, (3-5)% Cu, <0.6% Mo, $(5 \cdot C - 0.45)$% Nb.

Non destructive evaluation of the welded joints was performed with the aid of FPI (Fluorescent Particle Inspection which is a method involving penetrant). The essence of FPI is that fluorescent powder particles are retained inside of discontinuities which are opened towards the surface and are subsequently detected upon exposure to Ultra Violet light. As a result – defects invisible during standard visual inspection become visible as it has taken place in the case discussed here in. The FPI sensitivity varies depending on the choice of particular method. Standard FPI applicable to welded joint inspection did not reveal any defects, however when high sensitivity method was applied – some of them were detected. The results indicated the existence of linear defects in the HAZ adjacent to the fusion line. Further investigation proved that visual inspection using a borescope with magnification of. 10-20x is often a more reliable method to detect the subject micro cracks than the FPI techniques.

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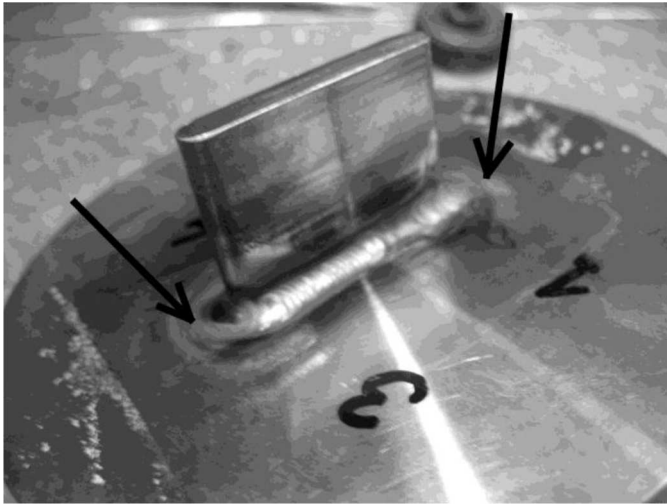** AMM EUROPE POLAND, ŚWIDNICA MANUFACTURING FACILITY

Fig. 1. Example of test weld joint configuration. Areas where cracking occurred most often (fillet weld curvatures around the member plate) are pointed with arrows

However, both FPI and visual detection techniques were limited by local oxide scale in the affected HAZ. The oxide scale prevented visual observation of the metal surface beneath the oxide and the mechanical removal of the oxide usually involved removal of metal to a thickness exceeding the average depth of the micro cracks. The oxide scale itself was also often cracked or delaminated from the base material in some areas: features which sometimes retained penetrant and resulted in false indications. For these reasons the most reliable technique of micro cracks detection was by examination of metallographic cross sections of areas identified by stereoscope microscope (using up to 63x magnification). In order to characterise the cracks and investigate their origin, metallographic sections were prepared and examined with both: a light microscope and a Scanning Electron Microscope (SEM). Search results for possible preventative measures were outlined. Typical appearance of the observed defects is presented in Fig. 2.

2. Discussion of results

During the investigation performed at another research institute, it was concluded that the observed defects were cold cracks caused by a hydrogen embrittlement phenomenon. The preliminary acceptance of this hypothesis, led to investigation of all the possible sources of hydrogen contamination. The possible sources identified were: the GTAW shielding gas (argon), the cooling gas used for post weld heat treatment (argon), and excessive humidity in the air at the welding station or during the surface cleaning processes preceding the welding operations. The argon purity level was checked and found to be high: 99.999% (for both the shielding and cooling gases) which excluded these gases as the sources of

hydrogen contaminant. Excessive air humidity was also excluded since measurements showed results for relative humidity as low as 30% (winter time). Similarly, all the surface cleaning processes were found not to be a factor since they didn't supply moisture which would be source of hydrogen for embrittlement. Also they didn't supply hydrogen in any other form that could be a source of embrittlement.

Metallographic evaluation of the provided test specimens extracted from welded parts and weld-test samples showed that the cracks do not exhibit typical features of hydrogen induced cracks. Typical cold cracks induced by a hydrogen embrittlement mechanism consistently initiate at the fusion line, their internal surfaces are free from oxidation and the bottom of the crack would have a relatively sharp appearance.
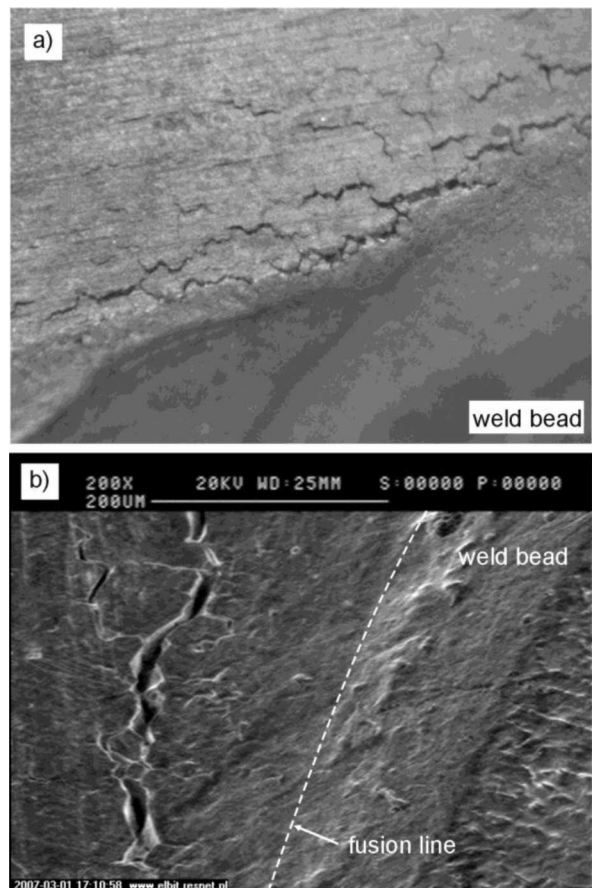

Fig. 2. Cracks in HAZ of 17-4PH steel welded with GTAW method a) cracks observed by stereoscope microscope, b) cracks observed by SEM

Figure 3 illustrates cracks on a metallographic section in the plane perpendicular to the base material surface and perpendicular to the fusion line. Cracks have an intergranular character (Fig. 4) and appear not only as adjacent to the fusion line but also at certain points in the HAZ away from the fusion line. They can be characterised by their significant width up to do 15 μm

and average depth of 50 μm. The internal surfaces of the cracks are oxidised and their bottom has form of a rounded wedge. The significant width and rounded bottom lead to the conclusion that the cracks originated as a result of large plastic deformations. These observations indicate that cracking was taking place when the value of temperature of the HAZ was high enough to promote oxidation by air in contact with the hot metal surface. At the same time, large deformations must have resulted from stresses induced by the welded joint constraints. This evidence has led to us to reject the hydrogen embrittlement hypothesis of the cracking mechanism and resulted in a new hypothesis stated that the observed defects are hot cracks. Chemical analysis of the base material showed a very low level of sulphur (0.001÷0.003%), allowing us to eliminate sulphur as a factor in the hot cracking mechanism in the HAZ.
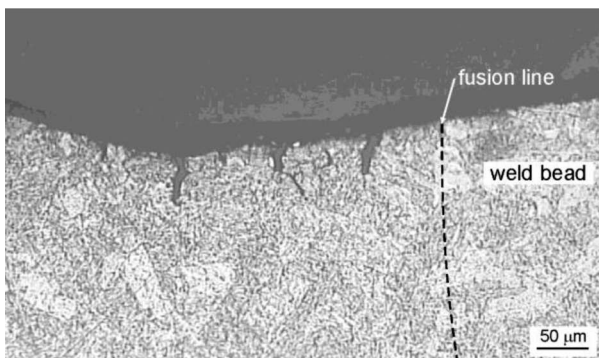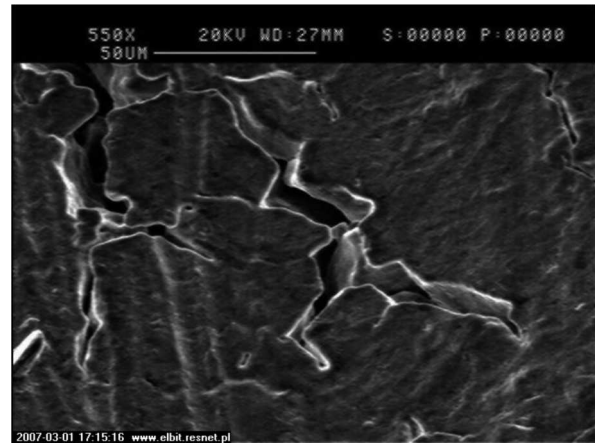

Fig. 4. Intergranular character of cracks in the HAZ. Significant width of the cracks is distinctive

In spite of welding in a protective atmosphere of very high purity shielding argon in the so called "argon balloon", the steel surface in the HAZ was discolored (Fig. 5). Titanium sample piece welded in the same conditions was not discolored in the HAZ. It demonstrates that the argon used as a protective atmosphere was of high purity and that the dark tarnish on the 17-4PH steel surface is not a result of oxidation processes resulting in oxide scale formation. Chemical microanalysis (using SEM Energy Dispersive X-Ray EDX) in the area of HAZ (Fig. 5b) and beyond the HAZ (Fig. 5a) has shown a distinct enrichment of copper in the HAZ area. Similar martensitic steels which do not contain copper (e.g. X3CrNiMo13-4) do not exhibit the susceptibility to the formation of micro cracks that is observed in the HAZ of 17-4PH steel, which contains 3÷5% of Cu. These observations have led us to the hypothesis that the presence of Cu is a primary cause of the hot crack formation.

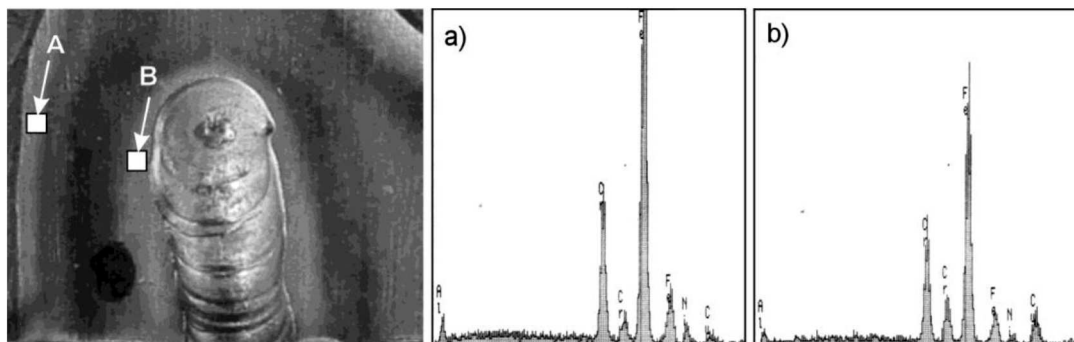

Fig. 3. Intergranular character of cracks in the HAZ

Fig. 5. Colored tarnish in HAZ along with depiction of chemical microanalysis areas: a) microanalysis deriving from area A, b) microanalysis deriving from area B
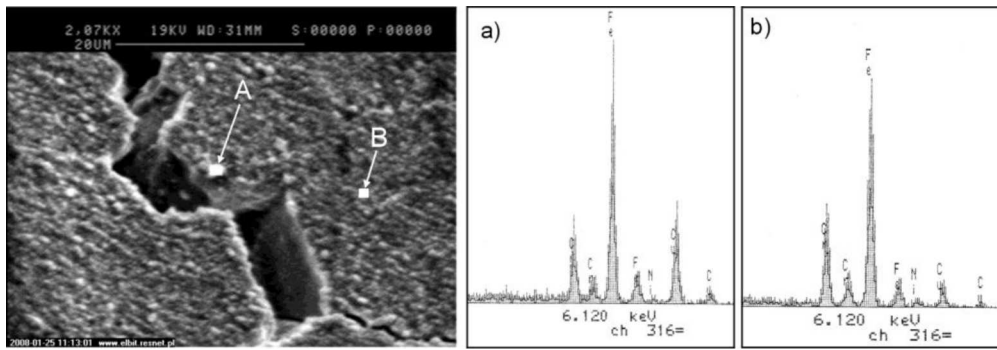
Fig. 6. Surface condition in the HAZ in the vicinity of the crack along with depiction of chemical microanalysis areas;
a) microanalysis deriving from area A (crack edge), b) microanalysis deriving from area B (slightly off-set from crack edge)
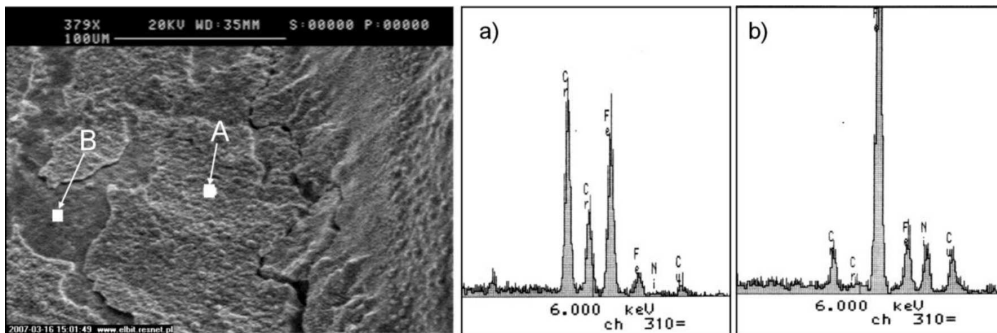

Fig. 7. Cracked and spalling oxide scale in the HAZ in the vicinity of the crack: a) microanalysis of the oxide scale (area A),
b) microanalysis of the base metal surface where scale was removed (area B)

Detailed analysis of the surface in the high temperature area of the HAZ has shown that the products deposited there have morphology typical of gas phase deposition (Fig. 6). The deposition products are enriched in Cu and depleted in Ni (Fig. 6b) when compared with the nominal chemical composition of the base material analyzed beyond the HAZ (Fig. 5a). Copper enrichment is especially pronounced at the edge of the crack (Fig. 6a).

In case of imperfect positioning of the welding torch, insufficient shielding of the welded area may occur resulting in the formation of a thick oxide scale. Oxide scale tends to crack and spall during base metal cooling. Fig. 7 shows an example of a thick layer of oxides. Microanalysis of the oxide scale and of the steel surface beneath the scale is also presented in Fig. 7. Microanalysis suggests that selective oxidation has taken place and formed oxides containing mainly Cr and Fe with small amounts of Cu (Fig. 7a). The steel surface underneath the scale is distinctively enriched in Cu and Ni and noticeably depleted in Cr (Fig. 7b).

The Cu content increase on the steel surface may be a result of the following:

- Selective oxidation of the steel,

- Evaporation and subsequent deposition of Cu from the weld pool.

Selective oxidation may occur in the event of incomplete protection of the steel surface from oxygen. Selective oxidation causes steel surface depletion in Cr, Mn and Si. Copper and nickel in the presence of Cr and Fe do not react with oxygen and therefore the steel surface under the oxide layer is enriched in Cu and Ni. An example of surface enrichment in Cu and Ni under the oxide layer is illustrated in Fig. 7. However, at the edge of the cracks and inside the cracks Cu enrichment and Ni depletion (in comparison with their nominal concentrations) are observed. If there is proper shielding the chemical composition in these areas cannot be a result of selective oxidation. Therefore the only explanation for steel surface enrichment in Cu is intensive evaporation of Cu from the weld pool. The boiling point of Cu is 2567°C and is lower than the boiling points of Chromium and Nickel; 2672°C and 2913°C respectively. Therefore during the welding process Cu is evaporating most intensively from the welding pool as a result of high temperature of the welding arc. Copper vapours are not freely released since they are entrained in the shielding gas flow and as a result they are directed towards the base metal surface where they are deposited by condensation in the cooler

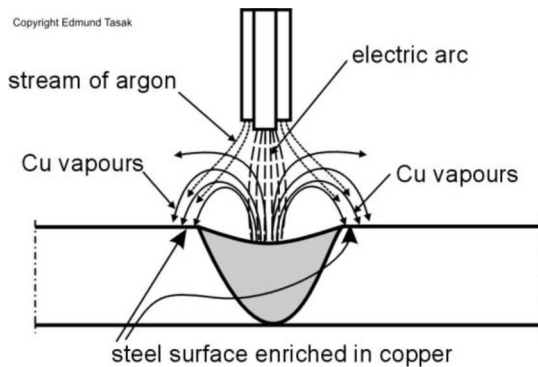HAZ area. Cu vapor deposition mechanism scheme is illustrated in Fig. 8.

Fig. 8. Mechanism of surface enrichment in copper in the HAZ area. Copper and Cu oxides vapours deposit and condensate

It is also possible that Cu vapours are being oxidised in the shielding gas stream and then Cu oxides would be deposited on the base metal surface. Melting point of Cu_2O is approx. 1200°C and for Cu_2O-Cu eutectic it is approx. 1065°C. Therefore, in the area adjacent to the weld bead, where temperature on the steel surface may reach around 1100°C a liquid layer of pure Cu or Cu_2O may be present. The weld shrinkage during cooling causes the development of stresses and that produce deformation of the material in the vicinity of the weld joint. This deformation in the presence of a liquid phase on the base metal surface results in a hot cracking phenomena. Small amount of liquid promote the development of shallow cracks – up to an observed maximum of 50 μm. The development of liquid phase on the base metal surface can be facilitated by relatively little Cu enrichment. Enrichment at the level of 8% of Cu is sufficient to develop liquid phase containing 97.2% of Cu (Fig. 9) as a result of incipient melting at 1094°C [4]. Therefore, even slight enrichment in copper may lead to development of a liquid phase rich in copper, which has a very high wettability of steel and causes hot cracks in the presence of tensile stresses. In the literature [5t÷8], this type of hot cracking in the presence of liquid metals is referred to as LME – Liquid Metal Embrittlement. It must be stated that without tensile stresses and the deformation caused by them – LME does not occur and base material is enriched in Cu by diffusion mechanisms.
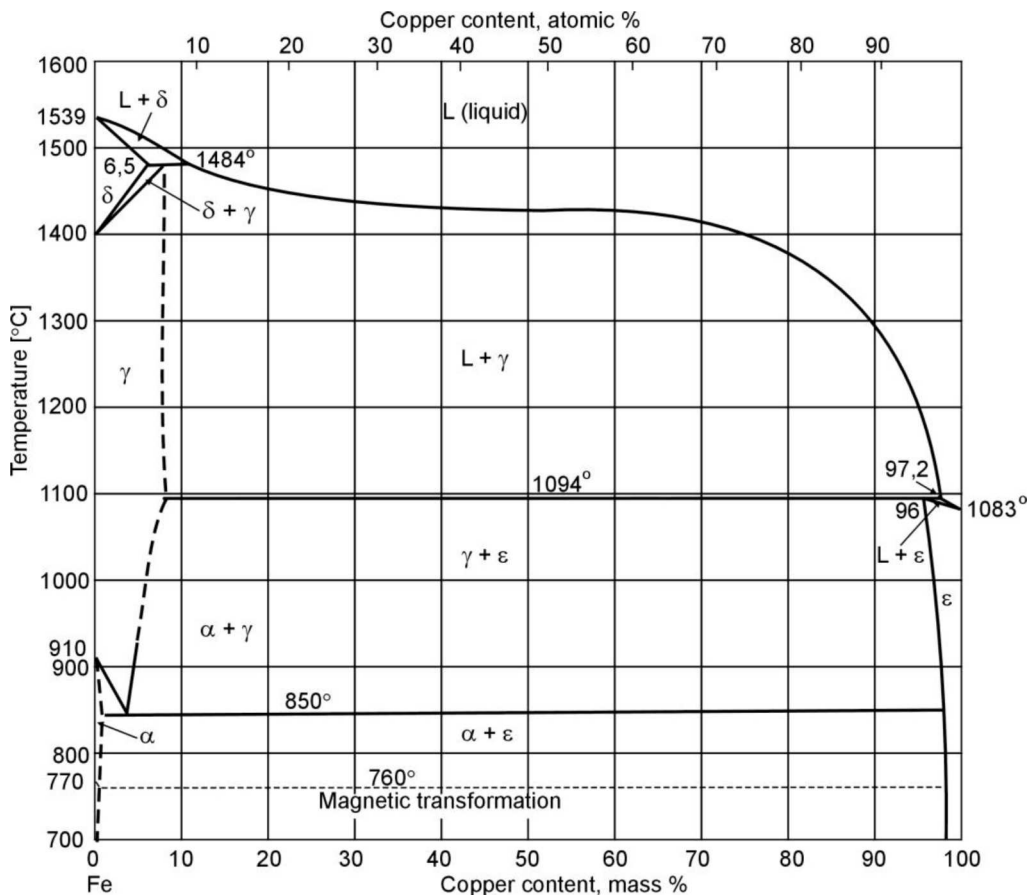

Fig. 9. Fe-Cu equilibrium diagram [9]

Welding process of 17-4PH steel using non-standard welding wires without Cu decreased the severity of cracking but did not prevent the phenomenon completely [10]. The cracks are difficult to detect due to their small depth and width. Among the NDT methods involving fluorescent particles – only the most sensitive inspections detected some of the defects. The presence of such cracks in highly loaded components may be a concern since they could lead to decreased fatigue cracking resistance. Presently there are no metallurgical methods to avoid cracking in the HAZ of steels that are precipitation hardened by Cu rich particles. The only way to eliminate the cracks is by their mechanical removal by polishing or by remelting the edge of the weld bead by GTAW without adding filler metal [11].

3. Summary

Outlined research indicates that cracks which developed in the weld HAZ of precipitation hardening martensitic stainless steel (a 17-4PH grade containing copper as a main constituent of the strengthening phase) result from a Liquid Metal Embrittlement phenomena. LME occurs when steel is subjected to tensile stresses in the presence of a liquid phase (Cu-rich in this case) on the surface. Under the influence of the very high temperature of the arc during the welding of 17-4PH steel, copper is the element that most intensively evaporates from the weld pool. The boiling point of Cu is 2567°C and is lower than boiling points of chromium or nickel; 2672°C and 2913°C, respectively. Cu vapors are not freely released since they are entrained in the shielding gas flow and directed towards the base metal surface where they are deposited by condensation in the cooler HAZ area. Development of liquid phase on the base metal surface can be produced by relatively little Cu enrichment. As a result of equilibrium incipient melting, enrichment at the level of 8% of Cu at 1094°C is sufficient to develop a liquid phase containing 97.2% of Cu. Therefore, even slight Cu enrichment may lead to the development of the liquid phase rich in copper, which has very high wettability of steel and causes hot cracks in the presence of tensile stresses.

In the case of insufficient protection of the welding arc by the shielding gas, it is also possible that Cu vapours emerging from the weld pool are oxidised and deposited on the surface as Cu_2O. The melting point of Cu_2O is approximately 1200°C and for the Cu_2O-Cu eutectic it is approximately 1065°C. Therefore, in the area adjacent to the weld bead, where the temperature on the steel surface may reach to around 1100°C a liquid layer of pure Cu or Cu_2O may be present. The weld shrinkage during cooling causes the development of stresses and deformation of the material in the vicinity of the weld joint. This deformation in the presence of liquid phase on the base metal surface results in a hot cracking phenomenon. The critical stress needed to cause steel hot cracking in the presence of liquid Cu on its' surface is approx 12MPa (1,74ksi) at 1100°C [12].

The observed smooth surface of the steel and the intergranular character of the cracks are characteristic of LME therefore supporting the hypothesis concerning the presence of liquid phase on the base metal surface. As thickness of liquid phase layer is small, it promotes the development of shallow cracks – up to observed maximum of 50 μm.

4. Conclusions

1. Cracks developing in the HAZ area of 17-4PH steel welds exhibit characteristics of hot cracks caused by steel embrittlement in the presence of liquid phase (LME – Liquid Metal Embrittlement).
2. Hot cracks in the HAZ can be eliminated by:
   - Removal of Cu vapour from the welded joint area;
   - Perfect protection of the welding zone from oxygen (especially in areas where weld beads overlap and in areas where welding direction is changed);
   - Reducing shrinkage stress and associated deformations.
3. If it is not possible to provide the preventive measures outlined above, the only solution to eliminate cracking is to change the base material from 17-4PH steelto one, such as PH 15-7Mo or 17-7 PH steel which have similar mechanical properties, but do not contain Cu.
4. Practical methods of cracks elimination are: mechanical polishing or GTAW remelting of the weld fusion line area without filler metal.

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