

Metal Interlayers To Prevent 'Hard Zone' Formation In Dissimilar Weldments Of Cr-Mo Steels – A Comparison Between Cu, Co And Ni

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ABSTRACT

High temperature exposure of dissimilar ferritic steel weldments either during service or during post weld heat treatment has been found to result in the formation of deleterious 'hard' and 'soft' zones near the weld interface. Activity gradient driven carbon diffusion was found to be responsible for the formation of the zones. One of the methods suggested for suppression of the zone formation is by use of carbon diffusion barriers. The effectiveness of this method was investigated in this study using numerical simulations based on finite difference method. Diffusion barriers like copper, cobalt and nickel were evaluated for this purpose due to their positive interaction parameter, ϵ_C^M with carbon. It was found that these interlayers if introduced between 9Cr-1Mo and 2¼Cr-1Mo ferritic steels reduce the propensity for formation of hard and soft zones. It was found by computation that their efficiency correlates well with the differences in interaction parameter with carbon.

and 2¼Cr-1Mo steels without interlayer, hard zone manifested as carbon enriched zone and soft zone as a carbon depleted zone. To predict the zone formation/suppression in a system carbon diffusion profiles have to be simulated for a specific time and temperature. The system under consideration in this study is a ternary system of Fe-M-C type where 'M' indicates any major substitutional alloying element like Cr, Ni or Mo. Since the activity of carbon is dependant upon chromium concentration the major alloying element considered here is Cr. When carbon diffuses due to the activity gradient from low Cr to high Cr side its concentration profile can be obtained using Fick's second law of diffusion. For ternary diffusion, Fick's second law can be rewritten using Onsager's formulation as⁶

$$\frac{\partial C_1}{\partial t} = \frac{\partial}{\partial x} D_{11} \frac{\partial C_1}{\partial x} + \frac{\partial}{\partial x} D_{12} \frac{\partial C_2}{\partial x} \quad (1)$$

$$\frac{\partial C_2}{\partial t} = \frac{\partial}{\partial x} D_{21} \frac{\partial C_1}{\partial x} + \frac{\partial}{\partial x} D_{22} \frac{\partial C_2}{\partial x} \quad (2)$$

1. INTRODUCTION

Ferritic steels are important class of structural materials for steam generator circuit of power plants due to their superior oxidation and creep resistance. When dissimilar weldments between ferritic steels are exposed to elevated temperature either during service or post weld heat treatment (PWHT) microstructural modification is observed at the weld interface. A precipitate free region called as the 'soft zone' of low hardness compared to rest of the weldment forms on the low alloy side and a precipitate rich region called as the 'hard zone' of high hardness forms on the high alloy side. Formation of such zones having different structure and property adjacent to each other near the weld interface is detrimental to the endurance of the component to thermal and mechanical stresses. Earlier studies¹⁻⁵ had suggested that activity driven carbon diffusion is responsible for the formation of these zones. Several methods have been suggested³ to prevent the formation of the zones such as (1) joining steels with graded Cr composition (2) adding elements like Nb, V or Ti that have higher affinity for carbon than Cr to the low Cr side and (3) using interlayers as diffusion barriers to carbon. Aim of the present work is to evaluate one of these methods i.e using diffusion barriers to prevent hard and soft zone formation in dissimilar weldments of 9Cr-1Mo and 2¼Cr-1Mo ferritic steels. Effectiveness of three different interlayers namely copper, cobalt and nickel has been investigated using numerical calculations based on finite difference method.

2. DETAILS OF NUMERICAL COMPUTATION

In carbon concentration profiles obtained using a microprobe⁴ across dissimilar weldment between 9Cr-1Mo

where C_1 and C_2 refer to carbon and chromium concentration in solution. D_{11} and D_{22} are the self-diffusion coefficients for carbon and chromium respectively. D_{12} and D_{21} are the cross diffusion coefficients, which take into consideration the effect of chromium on carbon diffusion. Using Schmit-method⁷, Onsager's equation for first order differential of concentration with respect to time $\left(\frac{\partial C}{\partial t}\right)$ and second order differential of concentration with respect to diffusing distance $\left(\frac{\partial^2 C}{\partial x^2}\right)$ can be transformed to finite differential equations. In the finite differential method only a one dimensional grid of mesh-points in space 'x' and time 't' is considered. The mesh points are separated by a space increment of Δx and time increment of Δt . After differentiation and transformation to finite differential form, eq. (1) and (2) for a particular grid point can be rewritten as shown below:

$$C_1[x,(t + \Delta t)] = C_1[x,t] + A + B \quad (3)$$

$$C_2[x,(t + \Delta t)] = C_2[x,t] + C + D \quad (4)$$

where

$$A = \frac{D_{11} \times \Delta t}{\Delta x^2} \{C_1[(x+1),t] - 2 \times C_1[x,t] + C_1[(x-1),t]\} \quad (4a)$$

$$B = \frac{D_{12} \times \Delta t}{\Delta x^2} \{C_2[(x+1),t] - 2 \times C_2[x,t] + C_2[(x-1),t]\} \quad (4b)$$

$$C = \frac{D_{21} \times \Delta t}{\Delta x^2} \{C_1[(x+1),t] - 2 \times C_1[x,t] + C_1[(x-1),t]\} \quad (4c)$$

$$D = \frac{D_{22} \times \Delta t}{\Delta x^2} \{C_2[(x+1),t] - 2 \times C_2[x,t] + C_2[(x-1),t]\} \quad (4d)$$

To calculate the change in carbon and chromium concentrations from eq. (3) and (4), self and cross diffusion coefficients should be known, which are calculated as follows:

Flux of a diffusing species can be written in terms of the activity gradient as⁸

$$J_C = -D_C \frac{\partial a_C}{\partial x} \quad (5a)$$

$$J_{Cr} = -D_{Cr} \frac{\partial a_{Cr}}{\partial x} \quad (5b)$$

where D_C and D_{Cr} are the activity diffusion coefficients of carbon and chromium respectively in the Fe alloy system. Here D_C and D_{Cr} are concentration independent constants and is equal to the diffusion coefficients of the species in a very dilute solution^{3, 9}. For ternary alloys activity of carbon a_C is given as

$$a_C = C_1 \left(\exp(C_1 \varepsilon_C^C + C_2 \varepsilon_C^{Cr}) \right) \quad (6a)$$

$$a_{Cr} = C_2 \left(\exp(C_1 \varepsilon_C^{Cr} + C_2 \varepsilon_{Cr}^{Cr}) \right) \quad (6b)$$

where ε_C^C and ε_C^{Cr} indicate carbon-carbon and chromium-carbon Wagner interaction parameters respectively.

Differentiating eq. (6a) and substituting for $\frac{\partial a_C}{\partial x}$ in eq. (5a)

gives the carbon flux ' J_C ' in terms of Wagner interaction parameter.

$$J_C = -D_C [1 + C_1 \varepsilon_C^C] \left[\exp(C_1 \varepsilon_C^C + C_2 \varepsilon_C^{Cr}) \right] \frac{\partial C_1}{\partial x} - D_C C_1 \left[\exp(C_1 \varepsilon_C^C + C_2 \varepsilon_C^{Cr}) \right] * \varepsilon_C^{Cr} \frac{\partial C_2}{\partial x}$$

Comparing the above equation with Fick's first law gives the diffusion coefficients as :

$$D_{11} = D_C (1 + \varepsilon_C^C C_1) \exp(\varepsilon_C^C C_1 + \varepsilon_C^{Cr} C_2) \quad (7)$$

$$D_{12} = D_C C_1 \varepsilon_C^{Cr} \left[\exp(C_1 \varepsilon_C^C + C_2 \varepsilon_C^{Cr}) \right]$$

$$\text{for } C_1 \varepsilon_C^C \ll 1 \quad D_{12} = D_{11} (\varepsilon_C^{Cr} C_1) \quad (8)$$

Similarly for the case of chromium diffusion we get

$$D_{22} = D_{Cr} (1 + \varepsilon_{Cr}^{Cr} C_2) \exp(\varepsilon_C^{Cr} C_1 + \varepsilon_{Cr}^{Cr} C_2) \quad (9)$$

$$D_{21} = D_{Cr} \varepsilon_{Cr}^{Cr} C_2 \left[\exp(C_2 \varepsilon_{Cr}^{Cr} + C_1 \varepsilon_C^{Cr}) \right] \quad (10)$$

To calculate the diffusion coefficients, values for the interaction parameters¹⁰ are substituted as $\varepsilon_{Cr}^{Cr} = -5$, $\varepsilon_C^{Cr} = -72$ and $\varepsilon_C^C = +1.33$. The concentration independent diffusion

coefficients D_C and D_{Cr} are taken as 1.05×10^{-11} m²/sec and 2.51×10^{-17} m²/sec respectively¹¹. Values for the diffusion coefficients D_{11} , D_{12} , D_{21} and D_{22} are then substituted back in eq. (4a) to (4d). Values for (C_1 , C_2) for 2¼Cr-1Mo and 9Cr-1Mo sides are taken as (0.12, 2.25 wt%) and (0.08, 10.25 wt%) respectively. Knowing the values of C_1 and C_2 for the mesh points x , $x+1$ and $x-1$ for a particular time ' t ', $C(x, t+\Delta t)$ can be calculated using eq. (3) and (4). Calculations were carried out in a one dimensional finite difference mesh with 100 mesh points with the following boundary conditions

$$C_1(x) = C_1(x+1); C_2(x) = C_2(x+1) \text{ at } x = 0$$

$$C_1(x) = C_1(x-1); C_2(x) = C_2(x-1) \text{ at } x = 101$$

$$\text{Flux, } D_{LHS} \frac{\partial C}{\partial x} = D_{RHS} \frac{\partial C}{\partial x}$$

The calculations were carried out keeping $\Delta x = 0.003$ mm and the criteria for the time increment as

$$\Delta t \leq \frac{\Delta x^2}{2D}$$

3. RESULTS

Figure 1 shows the carbon concentration profiles simulated across a dissimilar weldment between 2¼Cr-1Mo and 9Cr-1Mo steels subjected to PWHT at 1023 K for various time durations. Since the carbon content on both sides of the interface is the same (~0.1wt%), no change in carbon concentration profile is expected. However, there is a deviation from the conventional diffusion profile with redistribution of carbon observed on both sides of the weld interface. The carbon content decreases near the interface on 2¼Cr side forming a carbon depleted region of thickness ~50 µm (for 15 h). On 9Cr-1Mo side of the interface a carbon-enriched zone of thickness of ~20 µm forms. Such a behaviour has been observed when the carbon concentration was

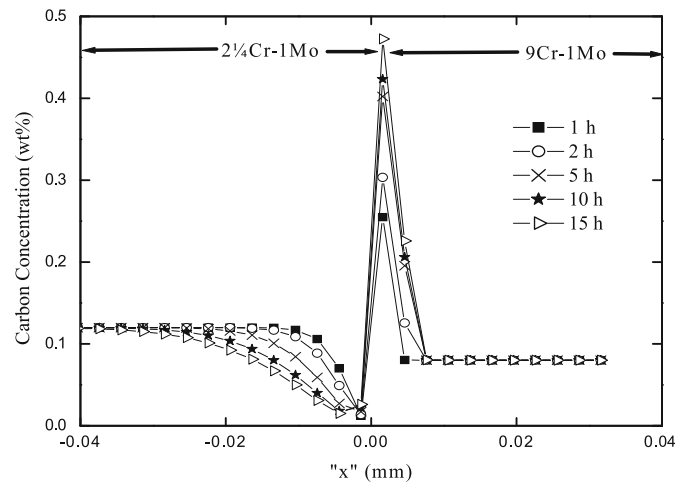


Fig. 1 : Carbon concentration profiles simulated across a dissimilar weldment between 9Cr-1Mo and 2¼Cr-1Mo ferritic steels for PWHT at 1023 K for durations ranging from 1 to 15 h ('x' is the distance from the interface in mm)

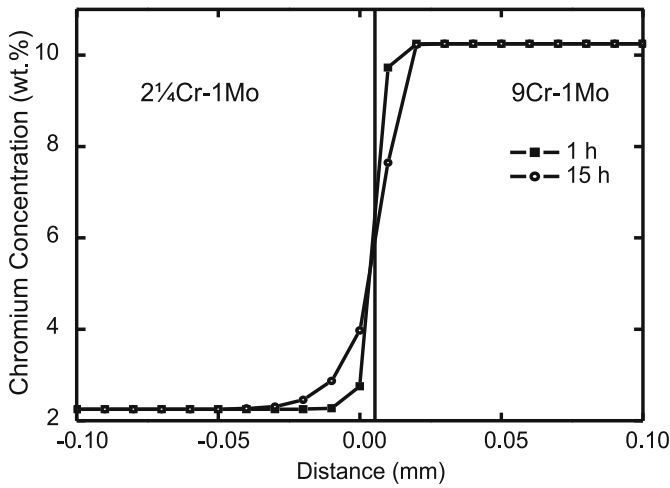


Fig. 2 : Chromium concentration profiles simulated across a dissimilar weldment between 9Cr-1Mo and 2 1/4Cr-1Mo ferritic steels for PWHT at 1023 K for 1 and 15 h ('x' is the distance from the interface in mm)

evaluated experimentally in the dissimilar weld⁴. The carbon depleted zone on 2 1/4Cr side and carbon enriched zone on 9Cr side have been found as soft and hard zones respectively. Figure 2 shows the chromium concentration profiles for PWHT at 1023 K for 1 and 15 h. The shape of the profile and increase in diffusion width with time are conventional signatures of diffusion profiles. It is also observed that there is interdiffusion of chromium very close to the interface.

Simulation of carbon concentration profiles was repeated by the same method for the dissimilar weld assuming various thicknesses of Cu, Co or Ni interlayer between 2 1/4Cr-1Mo and 9Cr-1Mo ferritic steels and subjected to the same conditions of temperature and time. For each interlayer, appropriate value was chosen for carbon content in solution, diffusion coefficient of carbon and the interaction parameter. From the carbon diffusion profiles the maximum carbon content in the hard zone was determined, which was used to optimize the thickness of interlayer required to suppress the formation of the zones. Figure 3 shows the variation of

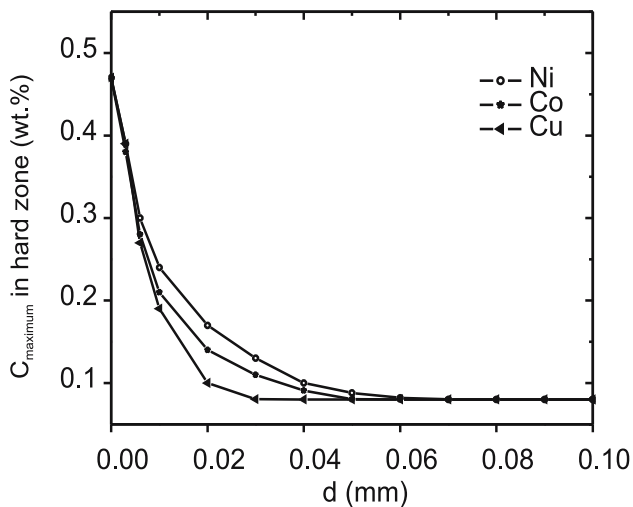


Fig. 3 : Variation of the maximum carbon content in the hard zone with thickness 'd' of three different interlayers in a dissimilar weldment between 9Cr-1Mo and 2 1/4Cr-1Mo ferritic steel for PWHT at 1023 K for 15 h.

maximum carbon content in the hard zone with thickness for the three different diffusion barriers. From the plot minimum thickness required for complete suppression of hard zone was estimated as ~40, 60 and 80 μm for copper, cobalt and nickel respectively.

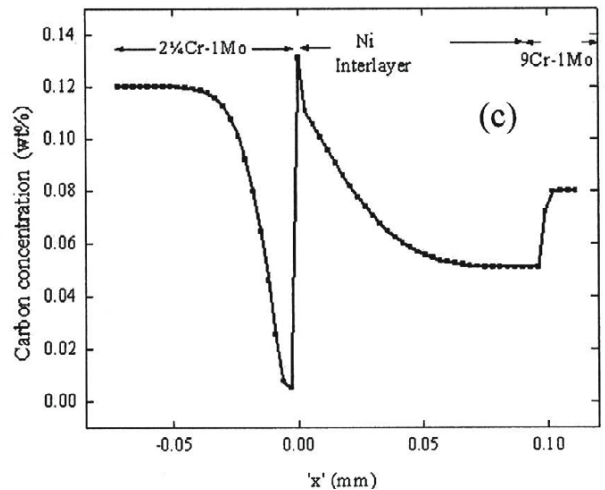
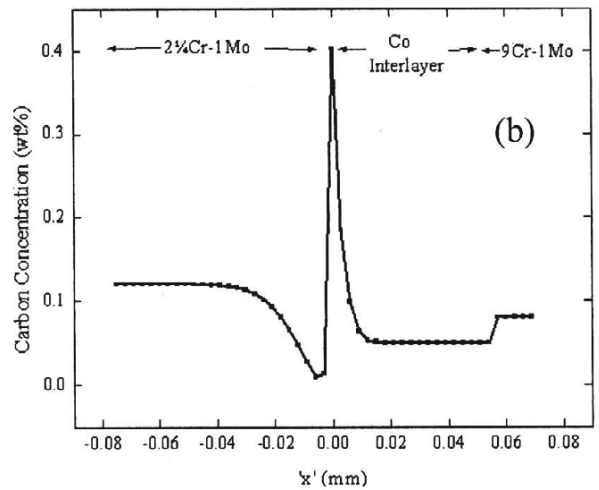
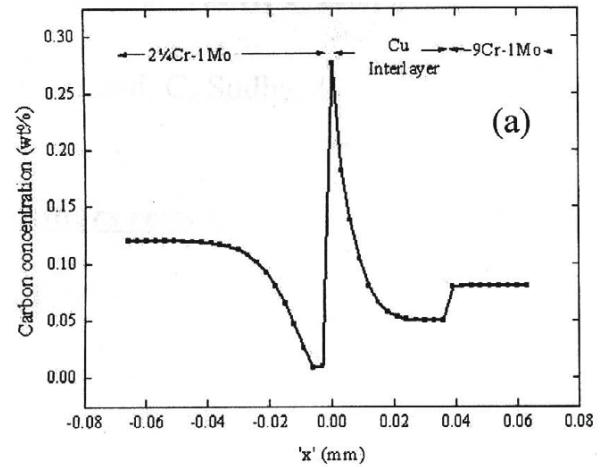


Fig. 4 : Carbon concentration profiles simulated across a dissimilar weldment with interlayer between 9Cr-1Mo and 2 1/4Cr-1Mo ferritic steels for PWHT at 1023 K for 15 h showing the absence of the zones. Profiles are generated for the optimum thickness of interlayer (a) Cu – 40 μm (b) Co – 60 μm and (c) Ni – 80 μm ('x' is the distance from interface in mm).

The carbon concentration profiles simulated across the dissimilar weldment using the optimized values of interlayer thickness are shown in Fig. 4(a) to (c). The propensity for the formation of hard zone near the 9Cr-1Mo interface is completely reduced by the introduction of the interlayer. Copper is found to be most effective in suppressing the hard zone formation followed by cobalt and nickel.

4. DISCUSSION

Diffusion of carbon across dissimilar weldments leading to the formation of 'soft' and 'hard' zones has been observed earlier¹⁻⁴. Formation of zones was explained based on the difference in carbon activity arising due to the interaction between carbon and the major substitutional alloying element namely chromium. Due to the activity gradient carbon diffuses from higher activity (low Cr) side to low activity (high Cr) side. Out of the different methods suggested³ the effectiveness of one of the methods to suppress the formation of these deleterious zones by introducing a diffusion barrier for carbon between the ferritic steels was investigated in this study. The effect of the interlayer in suppressing the hard zone formation was understood based on the interaction parameter of carbon and the constituent element of the interlayer, as is discussed below.

The criterion for choice of copper, cobalt and nickel as interlayer was based on their positive interaction parameter with carbon, which indicates a repulsive interaction. This introduces a large activation energy barrier at the interface between the interlayer and the ferritic steel, thus reducing the driving force for the diffusion of carbon. Consequently, diffusion of carbon from one side of the weld interface to the other side is prevented. This in turn prevents the formation of soft and hard zones during exposure of the weldment to elevated temperatures.

Calculations based on the finite difference method were used to simulate the carbon concentration profile across the weld interface. Carbon profile for a PWHT temperature of 1023 K for 15 h (Fig.1) in a dissimilar weldment between 2¼Cr-1Mo and 9Cr-1Mo ferritic steels showed the formation of hard and soft zones. It was observed that the zone formation was completely suppressed on introduction of the interlayer at the weld interface. Minimum thickness of the diffusion barrier

required to completely suppress the hard zone formation was found to be 40, 60 and 80 µm for copper, cobalt and nickel respectively. Table 1 shows a correlation between the interaction parameter ϵ_C^M and the optimum thickness of the interlayer required to suppress the zone formation. It is observed that the element with maximum value of interaction parameter is the most effective diffusion barrier. This suggests that, copper is the best choice for the interlayer as compared to cobalt and nickel.

Apart from the effectiveness in prevention of hard zone there are several other factors that have to be taken into account in the choice of an interlayer, such as compatibility with the base metal with respect to the melting point, thermal expansion coefficient and weldability. Nickel which has good weldability, similar thermal expansion coefficient and melting point as that of the ferritic steel is normally preferred compared to Cu and Co.

5. CONCLUSION

It was demonstrated through theoretical calculations that the formation of hard and soft zones in dissimilar ferritic steel weldments can be prevented using diffusion barriers consisting of elements like copper, cobalt and nickel which have a positive interaction parameter with carbon. The propensity for suppression of hard zone, inferred based on the minimum thickness required for suppression, correlates well with the variation of the interaction parameter.

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Table 1

Correlation between the interaction parameter and optimum thickness of interlayer required to suppress hard zone formation

S.No	Element	Interaction Parameter ϵ_C^M	Thickness of interlayer (µm)
1.	Cu	+3.5	40
2.	Co	+2.2	60
3.	Ni	+2.0	80