

고온고압장치 적용을 위한 9Cr-1Mo강 용접부의 연화특성에 관한 연구

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Study on Softening Characteristics of 9Cr-1Mo Steel Weldments for High Temperature and Pressure Vessels Application

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Key Words : 9Cr-1Mo Steel Weldments (9Cr-1Mo강 용접부), Soft Region (연화역), Heat Affected Zone (열영향부), Post Weld Heat Treatment (후열처리), Transformed Zone (변태역), Tempered Zone (뜨임영역), Carbide Precipitation (탄화물 석출)

초 록

고온고압장치(High Temperature and Pressure Vessels)의 적용을 위한 기초연구로서 9Cr-1Mo강 용접부의 연화특성에 대하여 검토하였다. 9Cr-1Mo 강재에 Bead-on-Plate 용접을 실시한 후, 용접부의 기계적성질과 그 현미경조직관찰 및 미세경도를 측정한 결과, As-Welded 및 용접 후열처리(PWHT)등의 조건에 관계없이 용접열향부의 변태역과 템퍼링역의 경계에서 모재의 경도보다 낮은 경도값(연화역)을 나타내었으며 이러한 원인은 결정립계(Grain boundary)에 석출되는 탄화물의 형성에 의한 뜨임 현상이 판명되었다.

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1. Introduction

Ferritic steels alloyed with chromium are utilized in applications where behavior or corrosion/oxidation resistance are necessary factor in materials selection. The typical use of these alloys has been in the power generation and process industries. With the advent of the nuclear power industry^{1,2)} and synfuels development programs^{3,4)} a world wide effort was initiated to develop materials with improved properties. Further, those industries historically using Cr-Mo alloys seek to employ higher pressure vessels which would result in increased economy and efficiency^{5,6)}.

Development of the 9Cr alloys was undertaken to eliminate ferritic to austenitic transition joint, to utilize the increased corrosion resistance compared to 2 1/4Cr and 3Cr materials, to obtain increased resistance to stress-corrosion cracking in caustic and chloride the use of strategic materials compared to 304 stainless steel, in particular chromium.

The principle criteria for alloy modification were to achieve creep properties that equalled or exceeded those of type 304 austenitic stainless steel up to 590°C and to maintain adequate weldability⁷⁾. These criteria have been addressed by the development of the Nb-V modified 9Cr-1Mo at ORNL¹⁾. The use of these modified alloys for pressure vessel applications requires that they be approved in the appropriate codes and standards (9Cr-1Mo-V-Nb has recently been approved for use by ASTM, A213-T91 for pipe and ASTM A387-Gr91 for plate).

Any decrease in hardness in the HAZ below the base metal hardness may be deleterious to the creep properties of a weldment. A decrease in hardness may be reflected by shorter times to failure at equivalent stress levels. Thus the HAZ may control the design of materials for elevated temperature behavior. Therefore, the mechanical properties and metallographic examination must be fully documented.

In this report, metallographic examination and hard-

ness measurements have been conducted on weldments of modified 9Cr-1Mo steel to determine the nature of base metal softening associated with HAZ.

This soft regions persist after Post Weld Heat Treatment(PWHT). An additional PWHT was performed to determine any effect of a subsequent PWHT on the degree of softening encountered in the tempered zone.

2. Softening Characteristics

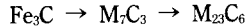
Softening in the welded joint has been observed in several ferrous materials. Easterling⁷⁾ reports that in plain carbon steels, the region for which the peak temperature in just below the A_1 experiences a transformation of pearlite to spheroidal Fe_3C and a concomitant decrease in hardness. Progrebnoi⁸⁾ has noted a softening in the HAZ of approximately 30 Hv below the base metal hardness for as-welded 11Cr-0.7Mo-0.35V steel. Challenger⁹⁾ has shown hardness decreases of 30 to 40 Hv in the HAZ of HY130. King¹⁰⁾ and Biss¹¹⁾ have shown hardness decreases in the HAZ below base metal hardness of between 10 and 30 Hv for modified 9Cr-1Mo and similar decreases for HT-9 and 2 1/4Cr-Mo alloys.

Poraebnoi and Biss^{8,11)} studied the carbide morphology using scanning electron microscopy. They found, when comparing the base metal and the softest region of the HAZ, that carbide coalescence had occurred with preferential carbide growth along the grain boundaries and, according to Biss, along the subgrain boundaries. Biss also studied the fusion zone and areas of the HAZ that had not been softened and found that carbide coalescence was the dominant factor in the softened region.

Challenger, et. al.⁹⁾ performed the most extensive study. Peak temperatures, heating rates, and cooling rates were measured at various locations in a multiple HY-130 weld HAZ. The locations in the HAZ corresponding to various peak temperatures were examined by optical microscopy, and transmission electron microscopy of carbide extraction replicas and thin foils.

The area of minimum softness was determined to correlate with rapid heating just below the A_{c1} (730°C). At this point both the extraction replicas and thin foils showed the presence of tempered carbides.

The general sequence of carbide formation in 9Cr-1Mo alloys is¹²⁾ :



The addition of niobium and vanadium may alter the kinetics of precipitation and growth of carbides in the 9Cr-1Mo alloys. The presence of niobium and vanadium results in the precipitation of both Nb and V rich MC type carbides¹²⁾. These MC type precipitates, present in a fine, dispersed form may act as nucleation sites for the precipitation of M_{23}C_6 resulting in a finely dispersed form¹³⁾. The presence of vanadium carbides of the V_2C_3 or VC type was not found in 9Cr-1.2% C steels with 0.4% V and 0.97% V by Seal and Honeycombe¹⁴⁾, but it was shown that the presence of vanadium in alloy restricts the diffusion of chromium in ferrite reducing the rate of carbide growth. This results in a lower extent of softening and minimizes the loss of strength upon tempering or PWHT.

The effect of vanadium in restricting the mobility of chromium may be an important factor in HAZ softening that occurs in the V-Nb Modified 9Cr-1Mo steels. If, during temperature excursions into the intercritical range, chromium mobility in the austenite is restricted while carbon partition to the austenite, a more rapid rate of tempering may occur during PWHT in the subsequently transformed martensite.

Thus, the studies to date have based on the conclusion that softening is the result of tempering on the position and/or shape of the carbides present and, while Challenger's study attempted to relate thermal history to the position of the softened region, it appears an exact temperature determination of a particular lo-

cation is difficult. Further, no attempt to determine the chemical composition or structure of the carbides in the softened region has been attempted.

3. Experiment

3.1. Material and Experimental Procedure

A heat of modified 9Cr-1Mo steel was utilized for the study of softening behavior. The materials were tested initially in the normalized and tempered condition (Normalized at 1040°C , tempered at 760°C , but some material was tested in the normalized condition at 1040°C) to get a better understanding of the HAZ and soft region.

Autogeneous single and multipass Gas-Tungsten-Arc (GTA) welds were deposited in the rolling direction using a heat input of 1.6kJ/mm.

Hardness measurements were then conducted on transverse sections of these welds to locate soft region and evaluate the extent of softening. In addition, the hardness measurements were conducted on specimens in the as-welded, PWHT conditions at 730°C for 1 hour and 10 hours.

Microhardness profiles were obtained across the HAZ in a direction perpendicular to the cross section. A Vicker's microhardness tester using a 2kg load was employed. The chemical compositions and welding conditions are shown in Table 1 and Table 2, respectively.

3.2. Metallographic Techniques

Metallographic specimens of the cross section weldments were prepared, metallurgically polished and etched with a reagent modified HCl-Picral and modified 5% Nital.

Table 1 Chemical Compositions of 9Cr-1Mo Steel (Wt. %)

Steel	C	Mn	P	S	Si	Ni	Cr	Mo	V	Nb	Ti	B
9Cr-1Mo-V-Nb	0.10	0.41	0.004	0.004	0.41	0.01	8.36	0.98	0.22	0.07	0.01	0.001

Table 2 GTA Welding Conditions

Variable	Setting
Welding	* GTA (AUTOGENOUS)
Plate Thickness	25 mm (1 in)
Current	220 Amps
Voltage	12 Volts
Travel Speed	3.5 in/min (9 cm/min)
Polarity	D. C. S. P
Interpass Temperature	Room Temperature
Energy Input	49 KJ/in

*GTA Welding : Bead on plate (100mm×30mm×25.4mm)

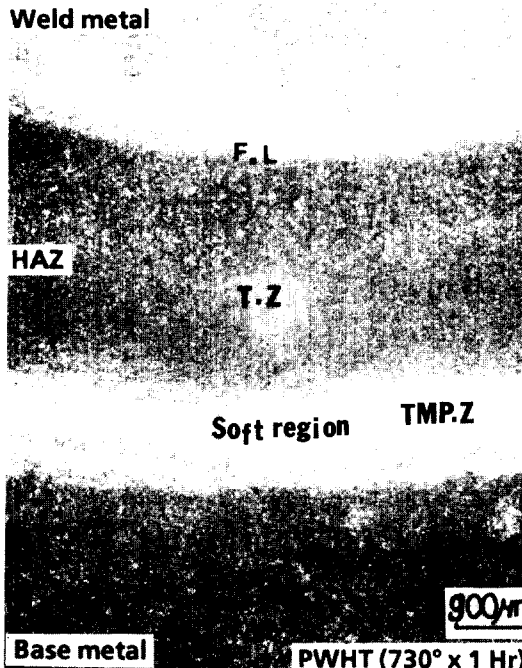
The HAZ called in this report is defined as the material between weld interface to unaffected zone, and a location of the base metal where the hardness is identical to that of the unwelded plate.

The HAZ consists of two subzones as illustrated by the low magnification optical micrograph shown in Photo. 1. The dark band labeled as T. Z. in Photo. 1 is defined as the transformed zone, where the peak

temperature of weld cycle is higher than designated the A_c1 . The region adjacent to the transformed zone, identified as TMP.Z, is defined as the Tempered Zone, which was exposed to temperatures below the A_c1 ; and was softened by tempering.

Optical light micrography, Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) were utilized to evaluate the role of carbide morphology.

Phase extracts for TEM studies were prepared from the tempered zone (soft region) of specimens by electrolytic dissolution of the matrix in 10% HCl-Methanol electrolyte at 1.3 volt, 1 amp. Also, chemical analysis



Phot. 1 Microstructure of bead on-plate weldment

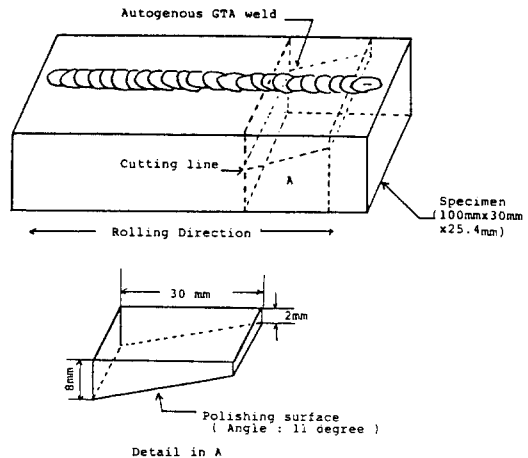


Fig. 1 Geometry of angle-cut specimen taken from autogeneows GTA weldment.

was STEM microscopies attached with micro-analyzer conducted to identify the carbide phase by the analysis of carbide extractions using IMAGE MASTER-TM.

So as to understand the extent and magnitude of the soft region characteristics, the angle cut specimens (Fig. 1) were prepared.

4. Results and discussion

4.1. Results

Photo, 2 shows the hardness traverse across the HAZ.

The hardness profile of the normalized and tempered modified 9Cr-1Mo-V-Nb steel for single pass, and five pass welds are shown in figures 2 and 3 respectively. It appears that a SOFT REGION exists in the HAZ, 3~3.5mm apart from the fusion line. The hardness of this soft region is 25~30 Hv lower than that of the base metal. However the PWHT at 730°C tends to eliminate this soft region.

The SEM Structures of weldments taken at various locations are presented in Photo, 3 (As-welded) and Photo, 4 (PWHT 730°C, 10 hr).

Slight coarsening and some agglomeration of carbides is evident in the microstructure at the location of lowest hardness(Photo. 3(d), 4(d)) as compared to the structure of the weld metal and HAZ (Photo. 3(b) (c) 4(b) (c)).

Hardness tests as those described above were conducted on the same material but in the normalized condition so as to exaggerate the extent and magnitude of the soft-region. Hardness traverses on single pass and five pass specimens are shown in Figure 4 and Figure 5 respectively.

The hardness profile of the modified 9Cr-1Mo-V-Nb steel in the normalized condition exhibits a pronounced 'Saw-Tooth' effect in the weld metal and transformed zone area (high temperature part of HAZ) reflecting the varying amounts of tempering and stress relief with location produced by the welding process.

The hardness of five pass weld drops sharply to

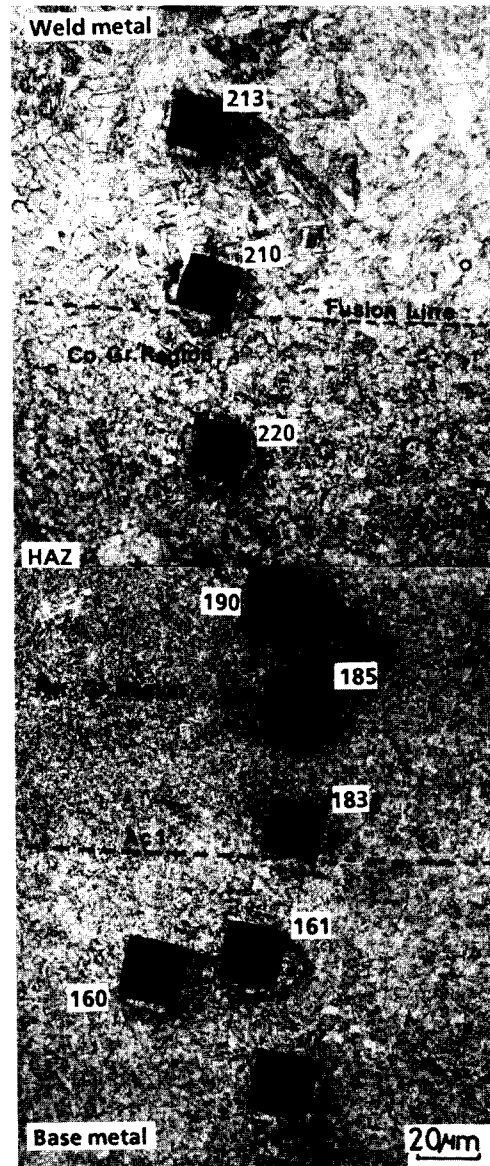


Photo. 2 Photograph of Micro-hardness test specimen

a low value of 250 Hv followed by a gradual hardness increase to the base metal hardness of over 420 Hv. The soft region hardness measure approximately 170 Hv and 200 Hv below that of the base metal in the single pass and five pass welds respectively. The location of the soft region appears to be closer to the fusion line in case of the five pass weld when compared to

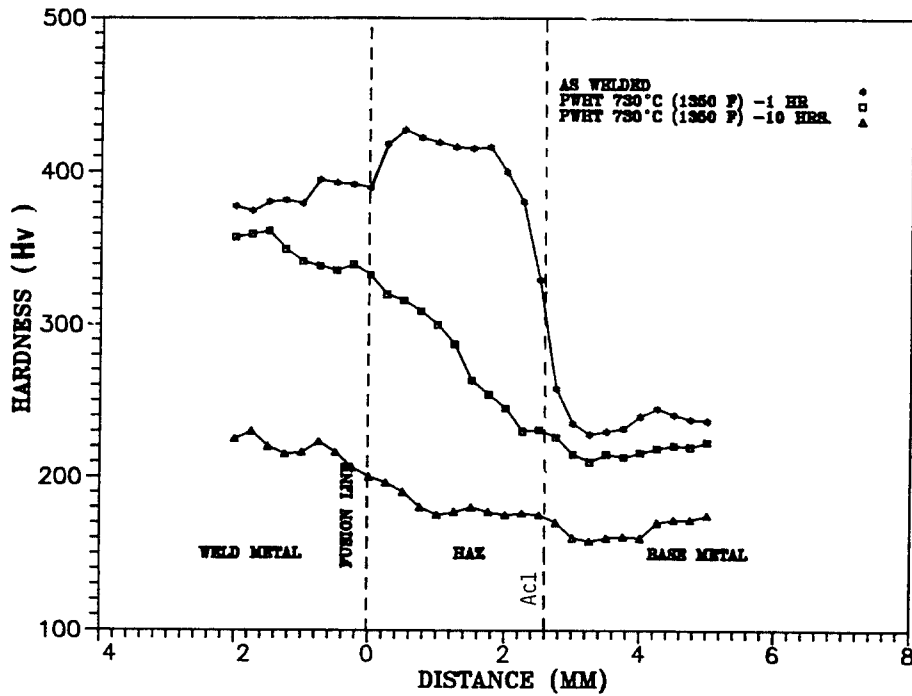


Fig. 2 Hardness distributions in transverse sections of single pass-welds in the normalized and tempered condition.

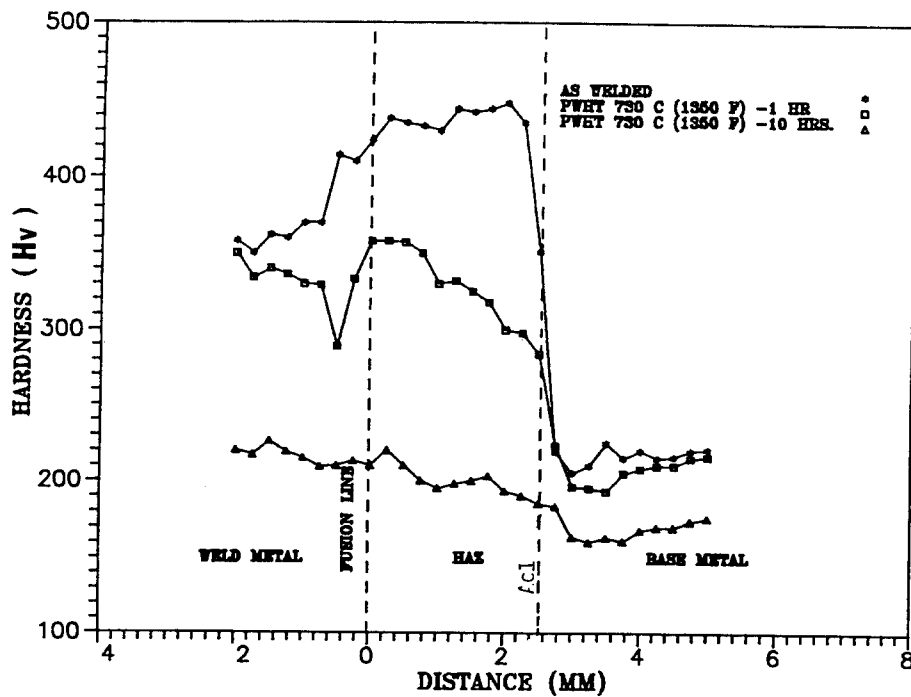


Fig. 3 Hardness distributions in transverse section of five passes welds in the normalized and tempered condition.

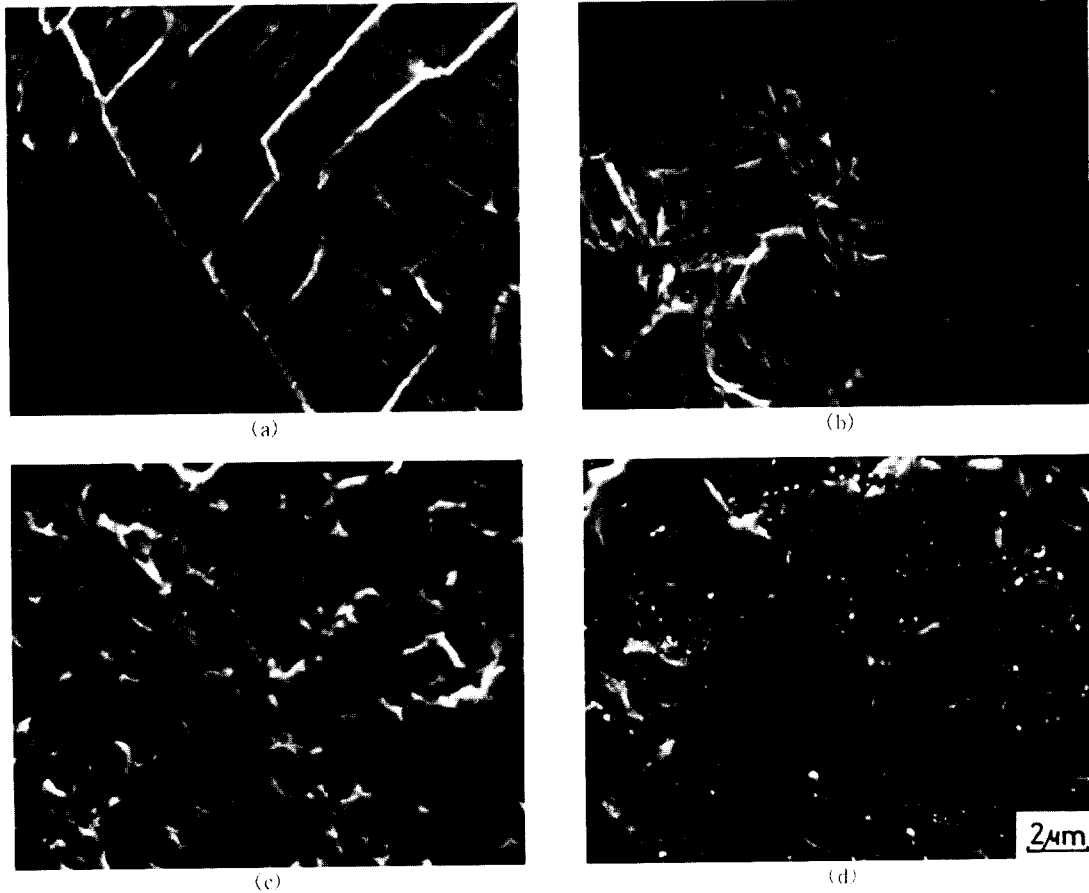


Photo. 3 SEM microstructures of (a) Weld Metal, (b) Coarse grained region of HAZ, (c) Fine grained region of HAZ, (d) Base metal near HAZ of normalized and tempered steel weldments (5 passes, As-welded condition)

the single pass weld. The location of the lowest hardness also coincided with the boundary between the transformed zone and the tempered zone.

The Micro-hardness profiles (Figure 6, Figure 7) of the angle cut specimens were similar to the hardness of normal cut specimens.

The microstructures of the angle cut specimens by scanning electron microscopy are shown in Photo. 5(a) and 5(b) for (N+T, 5 pass As-welded), Figure 6(a) and 6 (b) for (N+T, 5 pass PWHT 730°C, 1hr). The microstructures of the region having the lowest hardness (Photo. 5 Photo. 6) adjacent to the boundary bet-

ween the transformed zone and the tempered zone shows evidence of tempering characterized by the precipitation along grain and subgrain boundaries.

The carbide phases present in the soft region of weldment were identified as $M_{23}C_6$ as shown in Photo. 7, 8 and Figure 8, 9. In the $M_{23}C_6$ carbide, chromium is the major metallic component, and iron, molybdenum vanadium and niobium are present in lesser amount.

In comparison with normalized condition shown in Photo. 7, The N+T condition microstructure (STEM) of the soft region in the base metal near HAZ shown in Photo. 8 contain relatively larger amounts of very

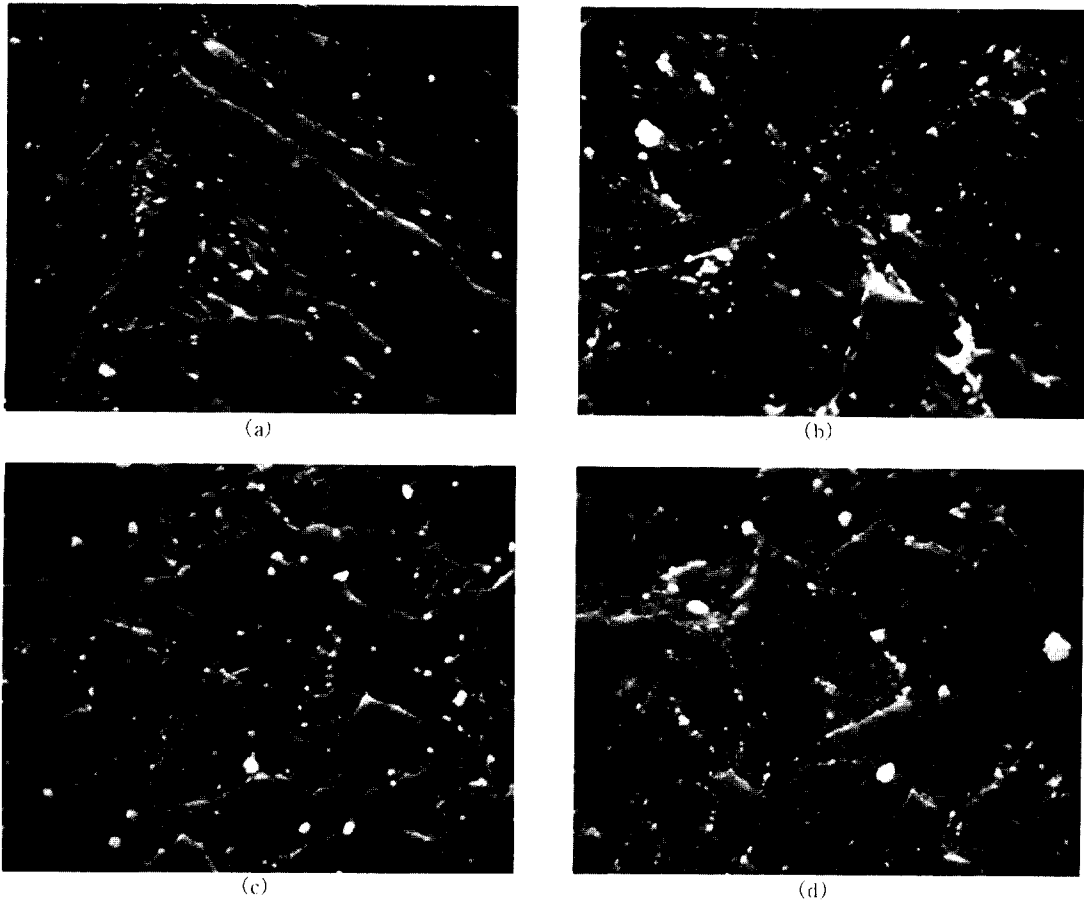


Photo. 4 SEM microstructure of (a) Weld Metal, (b) Coarse grained region of HAZ, (c) Fine grained region of HAZ, (d) Base metal near HAZ of normalized and tempered steel weldments (5 passes, 730°C×10hr PWHT condition)

coarsened carbide.

4.2. Discussion

The hardness profiles of the modified 9Cr-1Mo weldments in Figure 5 show that the highest degree of softening (about 170 Hv points) in the HAZ occurs in the normalized, as-welded steel weldment having relatively high hardness(about 400 Hv) both in the base metal and in the weld metal. However, since the modified 9Cr-1Mo steel is welded and used in the normalized and tempered condition, these results are not of practical significance, rather this untempered

condition was included for completeness.

The lowest hardness in the HAZ, 280 Hv, corresponds to that of produced by tempering this steel in the fully hardened condition at approximately 725°C for 1 hour. Tempering the base metal at 725°C before welding reduces its hardness to the 200~250 Hv range, and post weld heat treatment at 732°C for 1 hour reduced the hardness of the weld metal to a level slightly above that of the base metal. In the weldments with plates that had been normalized and tempered before welding the degree of softening in the location adjacent to the transformation zone is limited to about 25~30 Hv points below the average hardness of the

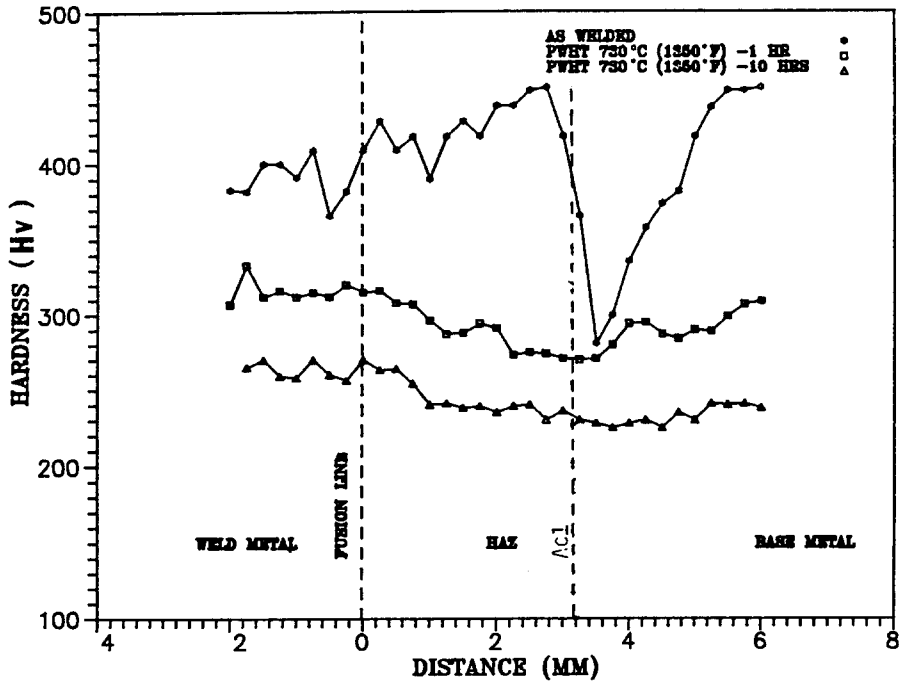


Fig. 4 Hardness distributions in transverse sections of single-pass welds in the normalized condition.

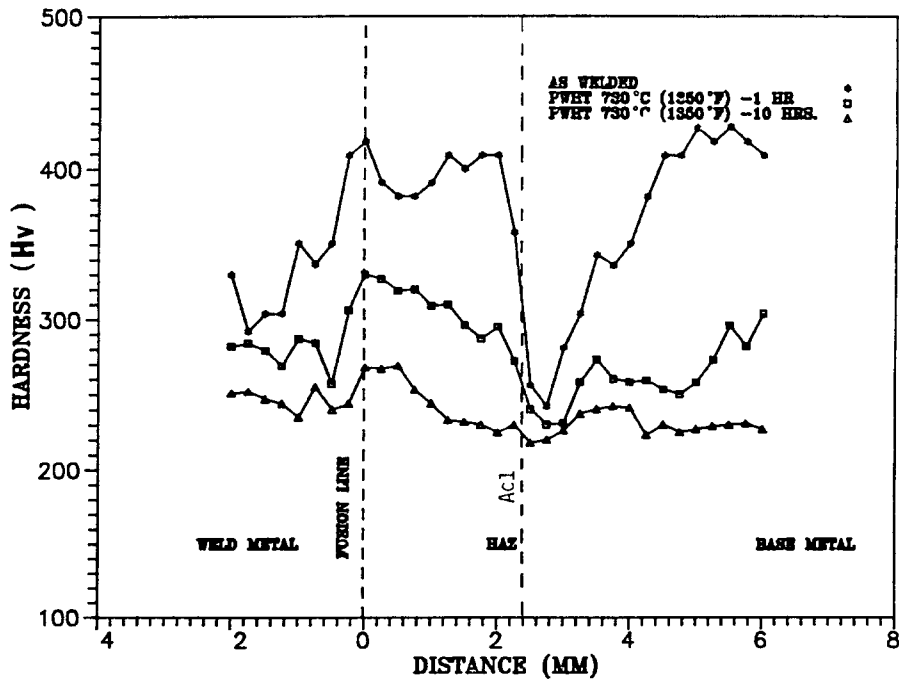


Fig. 5 Hardness distributions in transverse sections of five-passes welds in the normalized condition.

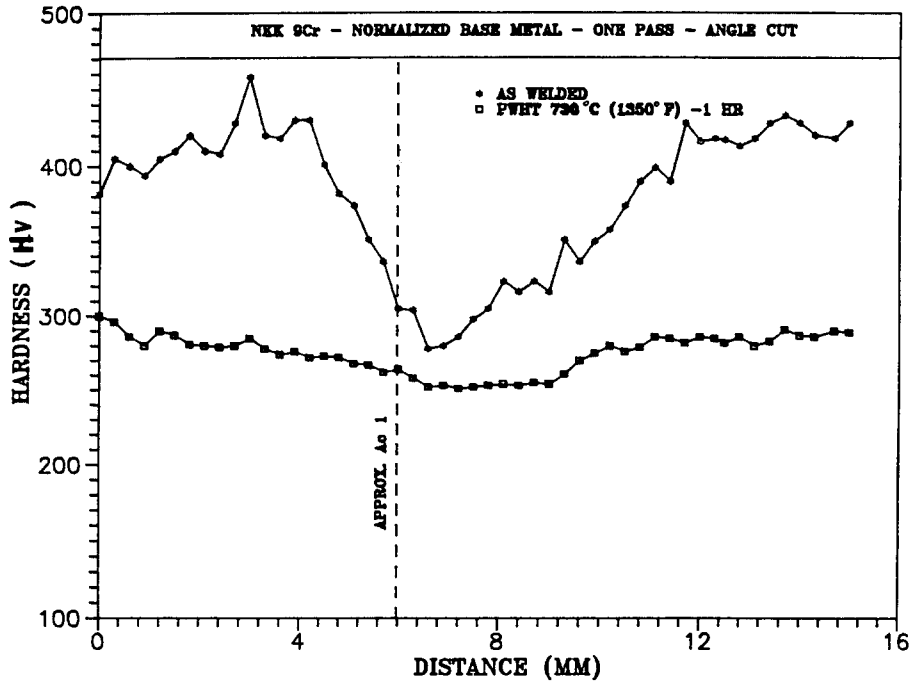


Fig. 6 Hardness distribution in angle-cut sections of single-pass welds in the normalized condition.

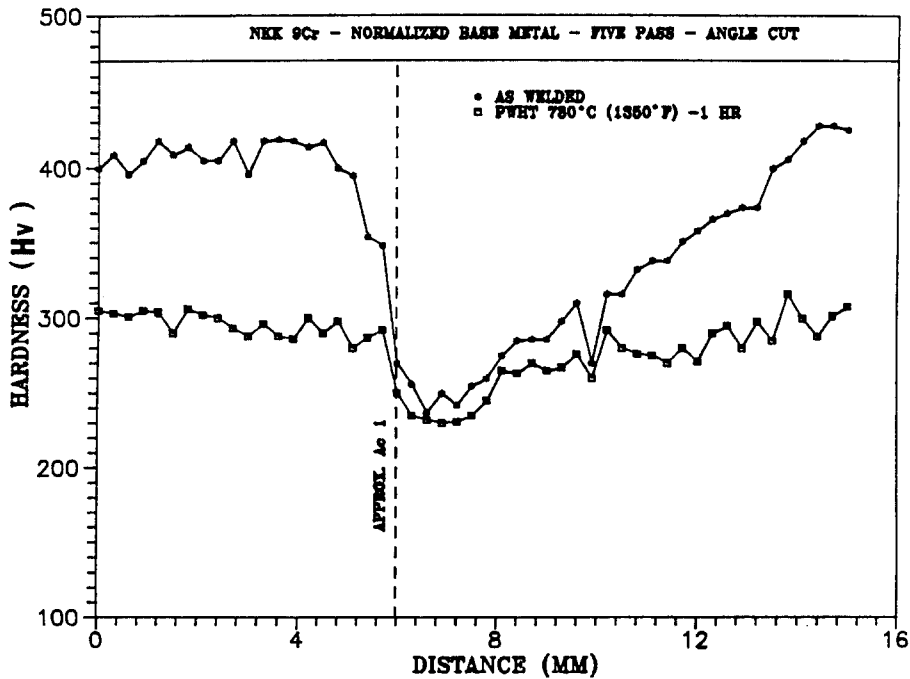


Fig. 7 Hardness distribution in angle-cut sections of five-passes welds in the normalized condition.

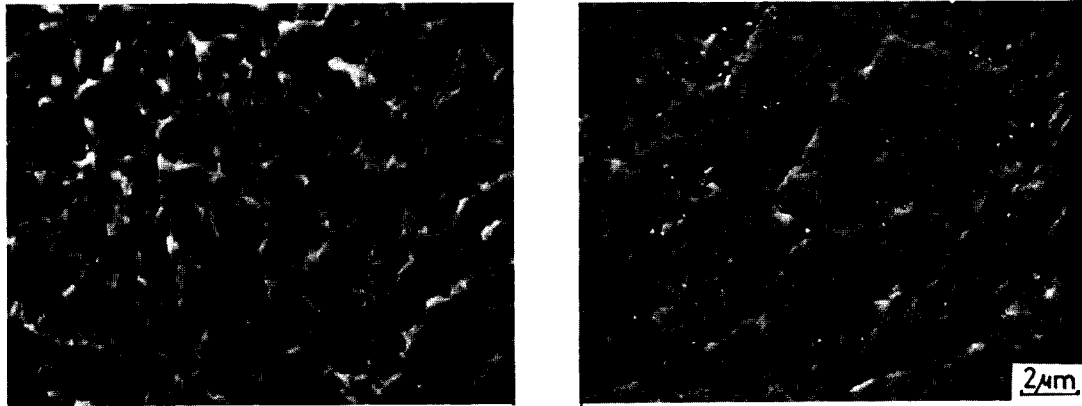


Photo. 5 SEM microstructures of (a) Fine grained region HAZ, (b) Base metal near HAZ of normalized and tempered steel weldments in angle-cut specimen (5 passes, As Welded)

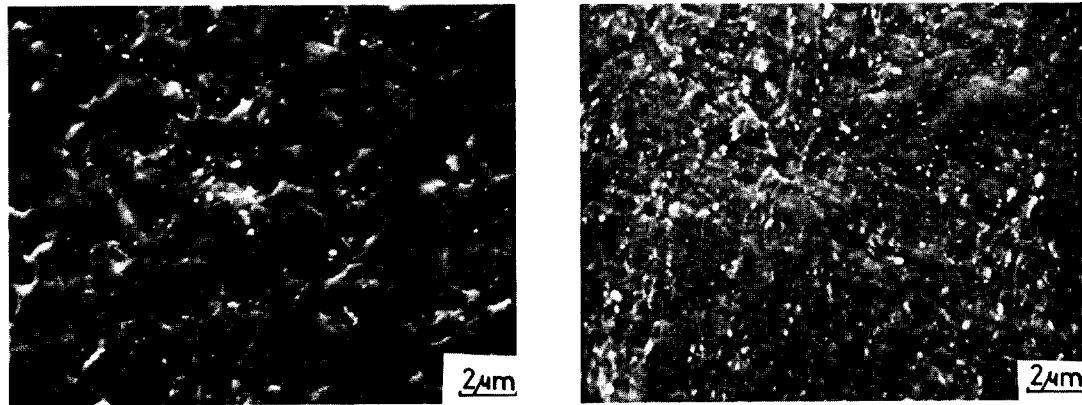


Photo. 6 SEM microstructures of (a) Fine grained region HAZ, (b) Base metal near HAZ of normalized and tempered steel weldments in angle-cut specimen (5 passes, 730°C×1hr PWHT)



Photo. 7 Scanning Transmission Electron Micrographs of Base Metal near HAZ in 9Cr-1Mo Steel weldmet, Normalized, PWHT 730°C×1hr, Angle-cut section.

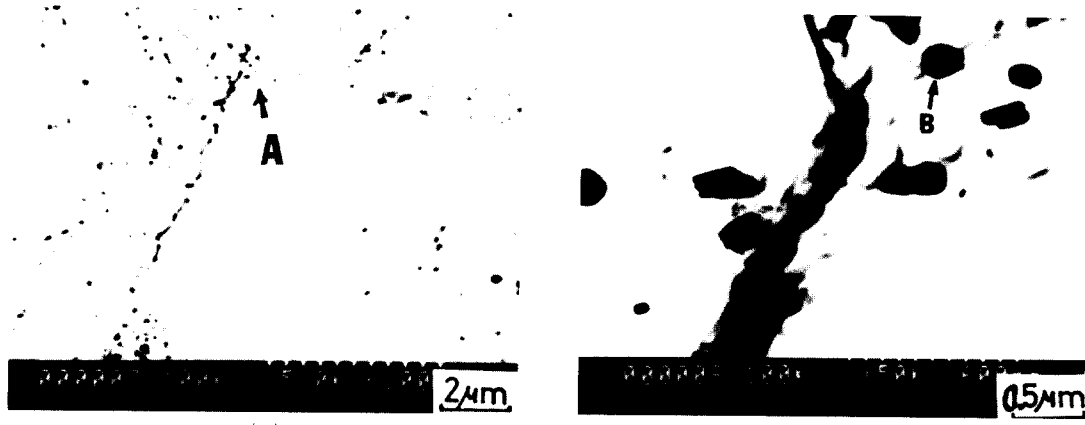


Photo. 8 Scanning Transmission Electron Micrographs of Base Metal near HAZ is 9Cr-1Mo Steel weldmet, Normalized and tempered, PWHT 730°C×1hr, Angle-cut section.

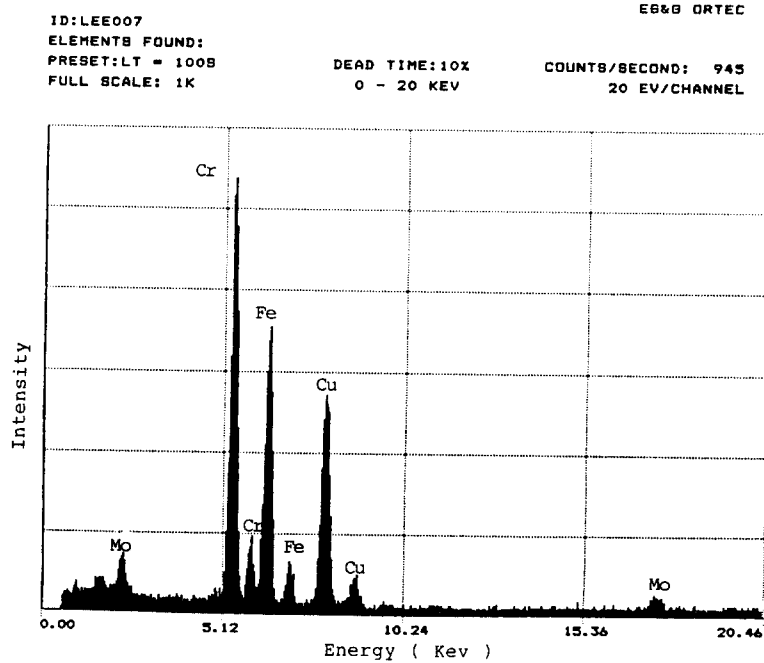


Fig. 8 STEM Micro-analysis of using this film approximation of the location b in Photo. 7(b)

same in the as-welded and post weld heat treatment conditions.

Comparison of these conditions with the tempering study of the same heat¹⁶⁾, reveals that minimum hardness in the HAZ of the weldment that was not tempe-

red after welding, 175 Hv, is approximately 25 Hv points below than produced by tempering at the Ac₁, 810°C for 1 hour. the lowest hardness in the HAZ of the weldment that was tempered after welding, 215 Hv, corresponds to that produced by tempering at approxi-

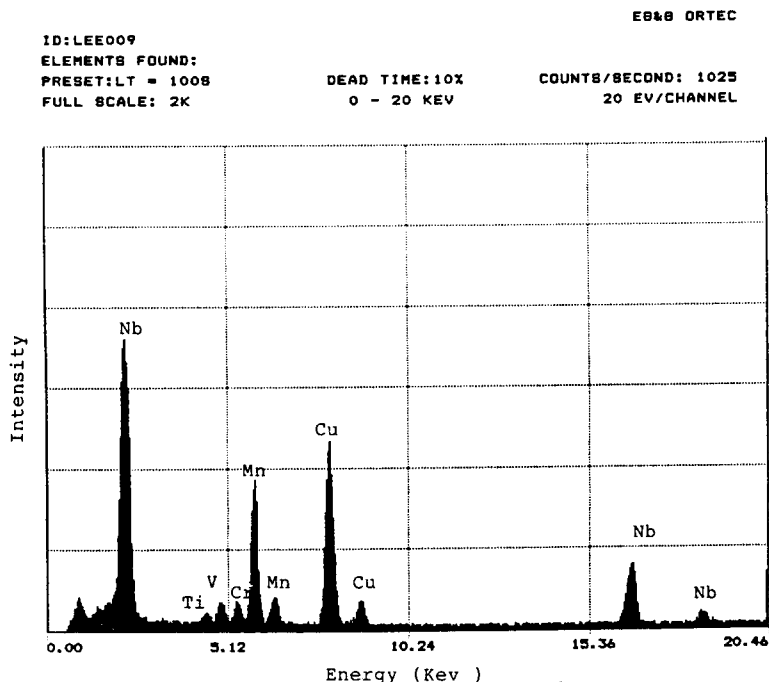


Fig. 9 STEM Micro-analysis of using this film approximation of the location B in Photo. 8(b)

mately 800°C for 1 hour.

The slight softening in the affected zone, adjacent to the transformed zone, of 9Cr-1Mo Steel is believed to be tempered effect from the heat generated in welding which results in a slight coarsening and agglomeration of the carbides.

Other contributing factors may be differences in dislocation density and cell size¹⁷⁾. The effects appears to be normal in chromium/molybdenum steel weldments and obviously poses no practical danger to welded structures as 9Cr-1Mo steel weldments have all been used successfully for many years.

5. Conclusions

The results of the investigation showed that the soft-region observed in the heat affected zone of 9Cr-1Mo-V-Nb(NKK) steel weldment is caused by slight coarsening of carbides due to the tempering effect imposed

by the heat generated during welding.

The main conclusions in this study can be summarized as follows ;

1. In the normalized and tempered modified 9Cr-1Mo-V-Nb steel weldments, the soft region existed in the outer region of HAZ, 3~3.5mm apart from the fusion line. The hardness of this soft region was slightly lower than that of the base metal in an extent of 25~30 Hv.
2. In the normalized condition, the hardness of soft region was 170~200 Hv and is lower than that of the base metal both in single pass and five pass welds.
3. The location of the soft-region appeared to be closer to the fusion line in case of the five pass weld compared to the single pass weld.
4. The hardness in the as-welded and post weld heat treatment condition decreased as a same degree.
5. The micro structures at the point lowest hardness adjacent to the boundary between the transformed zone and the tempered zone showed tempering cha-

racterized by precipitation of carbide along the grain and subgrain boundaries.

- The carbide phases present in the soft-region of weldment were identified as $M_{23}C_6$ type.

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