研 究 論 文

大 韓 熔 接 學 會 誌
第 10 卷 第 3 號 1992年 9月
Journal of the Korean Welding Society
Vol. 10. No. 3, Sep., 1992

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

이영호* · 이규천* · 윤의박** · 김기철***

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

Y.H.Lee*, K.C.Lee*, E.P.Yoon**, K.C.Kim***

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 현상임이 판명되었다.

* 정회원, 충남대학교 공과대학 기계공학과
** 정회원, 한양대학교 공과대학 재료공학과
*** 정회원, 산업과학기술연구소 용접연구센타

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].

Devleopment of the 9Cr alloys was undertaken to eliminate feeritic 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℃ and to maintain adequate weldability[2]. These creteria have been addressed by the development of the Nb-V modified 9Cr-1Mo at ORNL[1]. 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 hardness meaurements 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. Easterling[7] 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. Progrebnoi[8] 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. Challenger[9] has shown hardness decreases of 30 to 40 Hv in the HAZ of HY130. King[10] and Biss[11] 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 gorwth along the grain boundaries and, according to Biss, along the subgrain boundaries. Biss also studie 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. at.[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 Ac_1 (730℃). 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 is[12] :

$$Fe_3C \rightarrow M_7C_3 \rightarrow M_{23}C_6$$

The addition of niobium and vanadium may alter the kinetics of precipitation and growth of carbides in the 9Cr-1Mo alloys. The pressence of niobium and vanadium results in the precipitation of both Nb and V rich MC type carbides[12]. 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 form[13]. The presence of vanadium carbides of the V_2C_3 or VC type was not found in 9Cr-1.2%C steels with o.4%V and 0.97%V by Seal and Honeycombe[14], but it was shown that the presence of vanadium in alloy restricts the diffusion of chromium in feerite 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 attemped to relate thermal history to the position of the softened region, it appears an exact temperature determination of a particular location 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℃, tempered at 760℃, but some material was tested in the normalized condition at 1040℃) 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℃ 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 corss 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

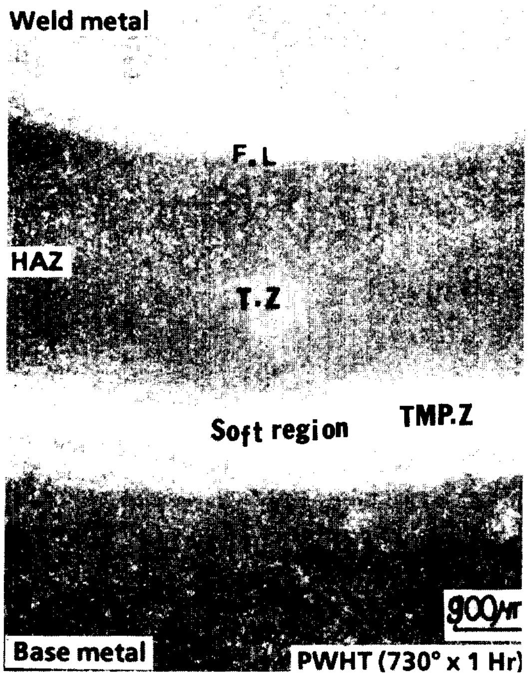
Table 2 GTA Welding Conditions

Variable	Setting
Welding	* GTA (AUTOGENOUS)
Pate 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 materal 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 in higher than designated the Ac_1. The region adjacent to the transformed zone, identified as TMP.Z, is defined as the Tempered Zone, which was exposed to temperatures below the Ac_1 ; and was softened by tempering.



Phot. 1 Microstructure of bead on-plate weldment

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

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

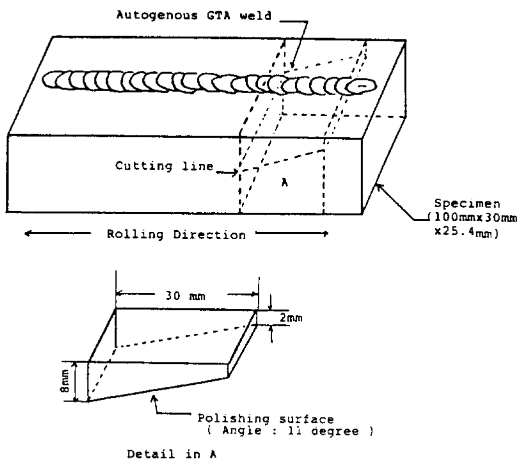


Fig. 1 Geometry of angle-cut specimen taken from autogeneows GTA weldment.

was STEM microscopies attached with micro-analizer 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 prpared.

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 form 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℃ tends to eleminate this soft region.

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

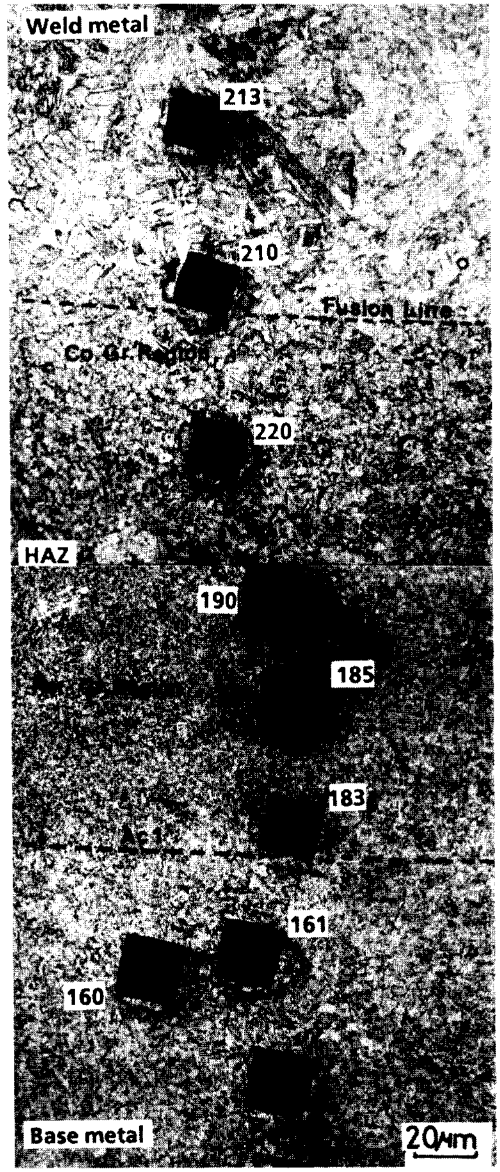


Photo. 2 Photograph of Micro-hardness test specimen

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 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 thd soft region appears to the closer the fusion line in case of the five pass weld when compared to

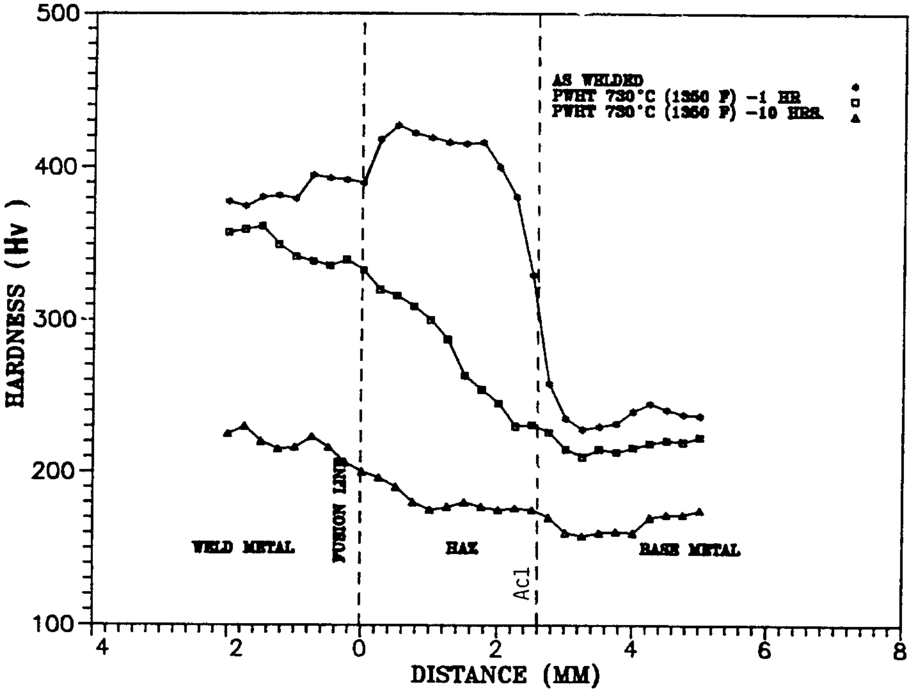


Fig. 2 Hardness distributions in transverse sections of single pass-welds in the normalized and ter.pered condition.

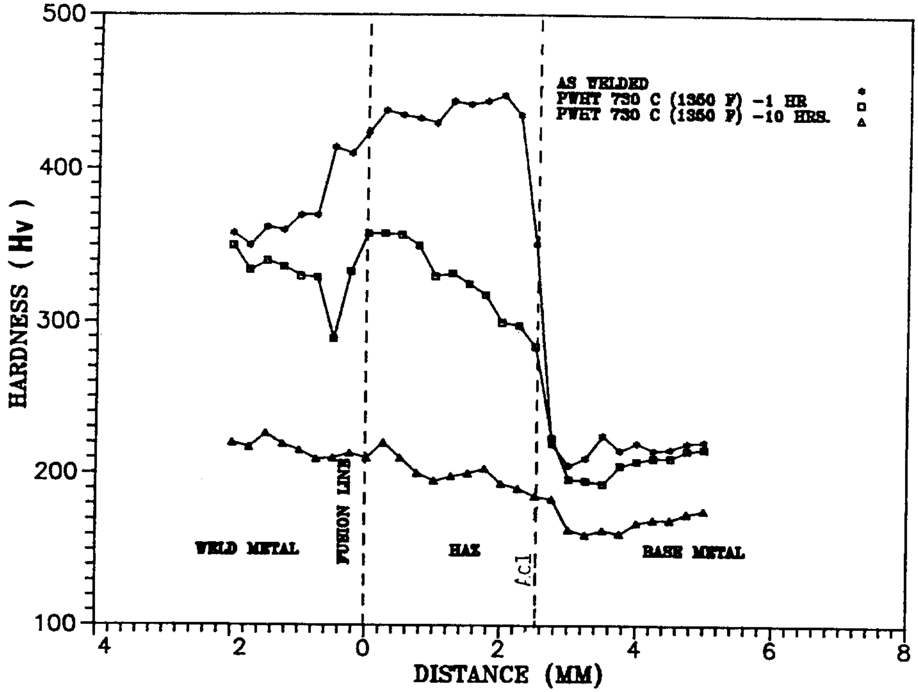


Fig. 3 Hardness distributions in transverse section of five passes welds in the normalized and tempered condition.

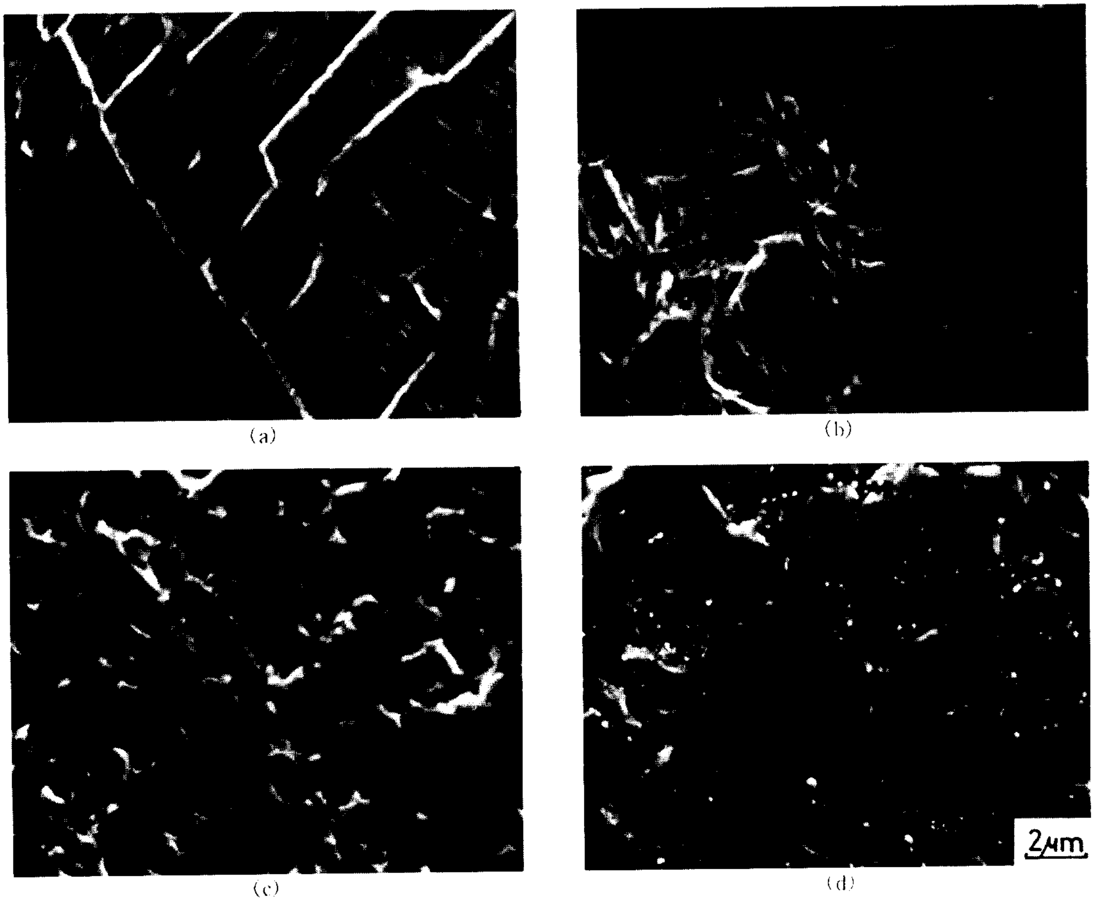


Photo. 3 SEM microstructures of (a) Weld Metal, (b) Coarse grained region of HAZ, (c) Fine grained region of HAZ, (d) Base metal near HAZ of normalized and tempered steel wedments (5 passes, As-welded condition)

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 spectmens 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℃, 1hr). The microstructures of the region having the lowest hardness (Photo. 5 Photo. 6) adjacent to the boundary between 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 largeramounts of very

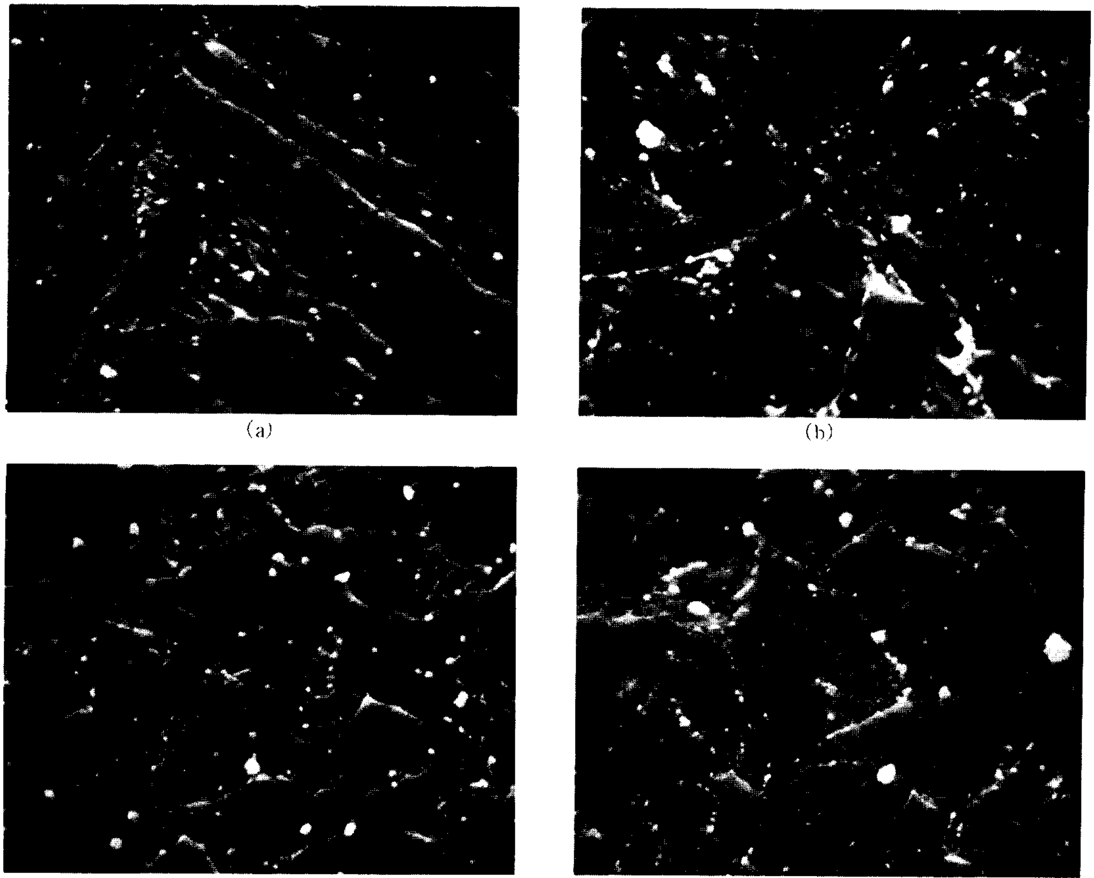


Photo. 4 SEM microstructure of (a) Weld Metal, (b) Coarse grained region of HAZ, (c) Fine grained region of HAZ, (d) Base metal near HAZ of normalized and tempered steel weldments (5 passes, 730℃ × 10hr PWHT condition)

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 normallzed 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 prodused by tempering this steel in the fully hardened condition at approximately 725℃ for 1 hour. Tempering the base metal at 725℃ before welding reduces its hardness to the 200~250 Hv range, and post weld heat treatment at 732℃ for 1 hour reduced the hardeness 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

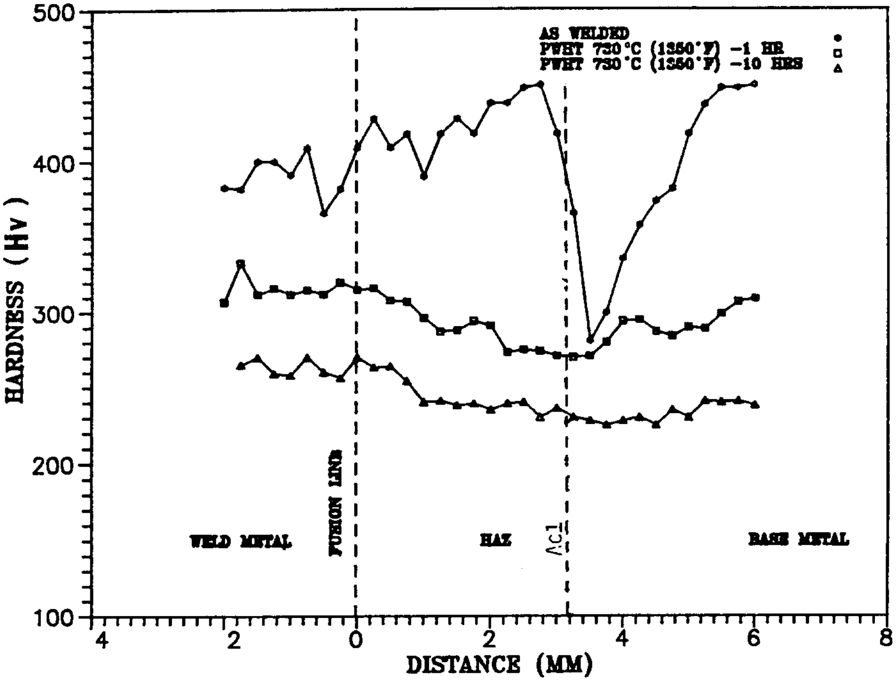


Fig. 4 Hardness distributions in transverse sections of single-pass welds in the normalized condition.

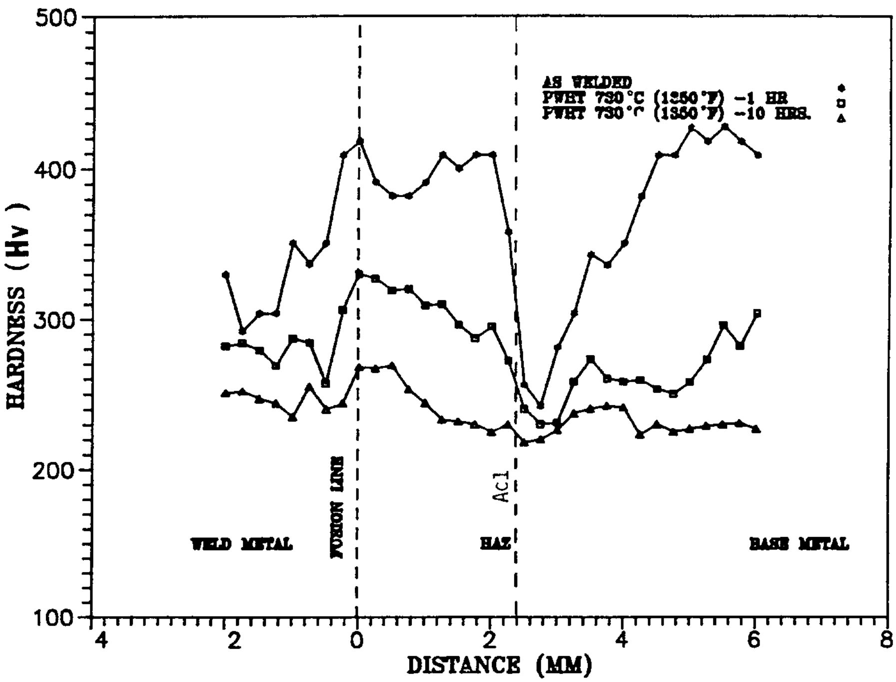


Fig. 5 Hardness distributions in transverse sections of five-passes welds in the nomalized condition.

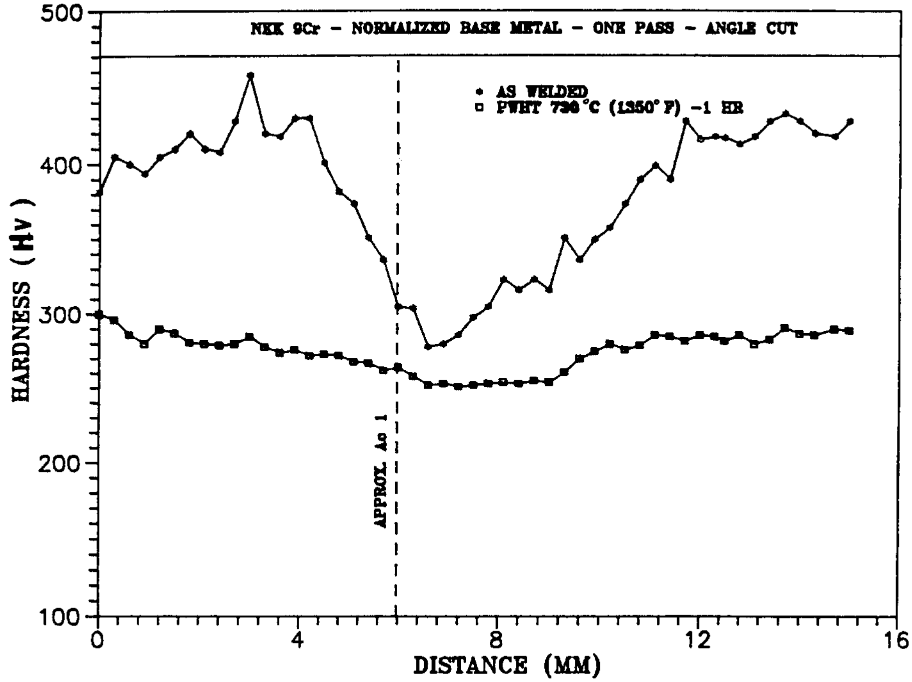


Fig. 6 Hardness distribution in angle-cut sections of single-pass welds in the normalized condition.

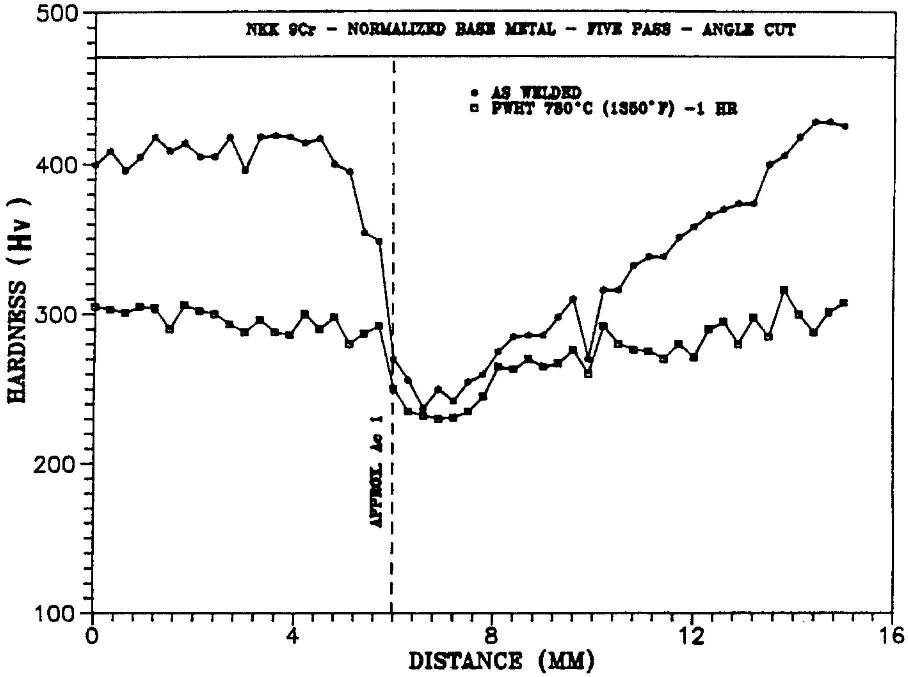
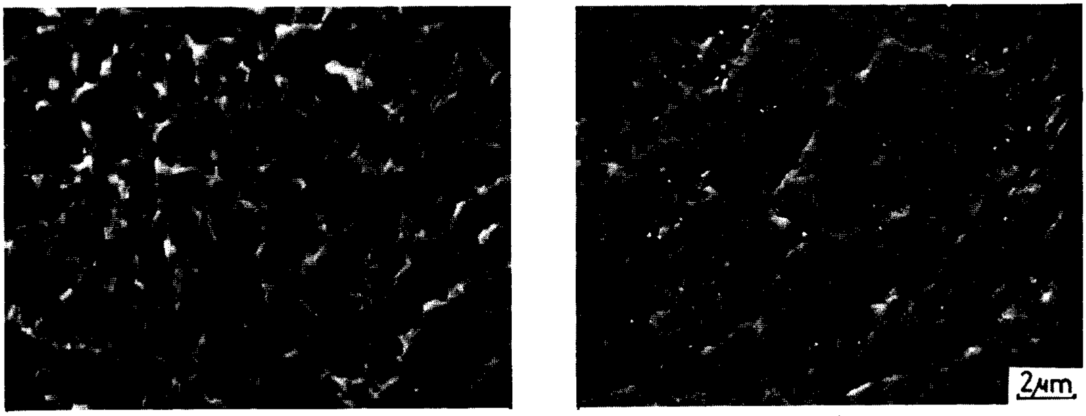
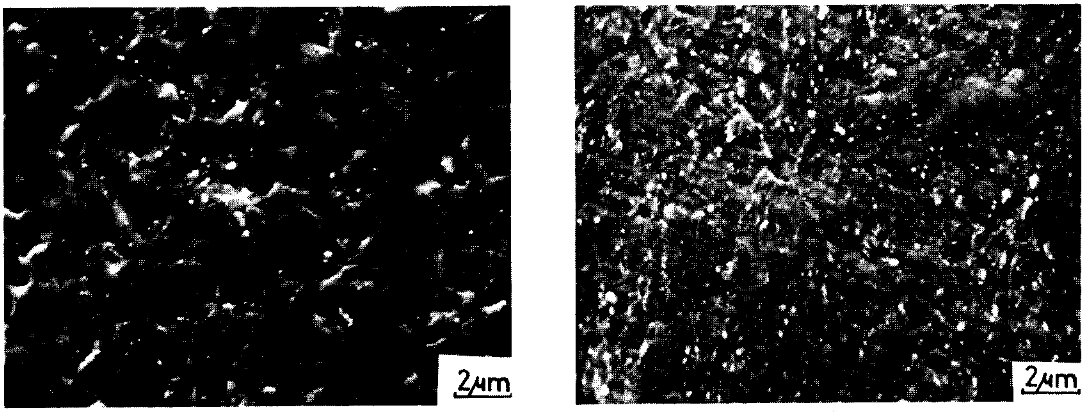


Fig. 7 Hardness distribution in angle-cut sections of five-passes welds in the normalized condition.



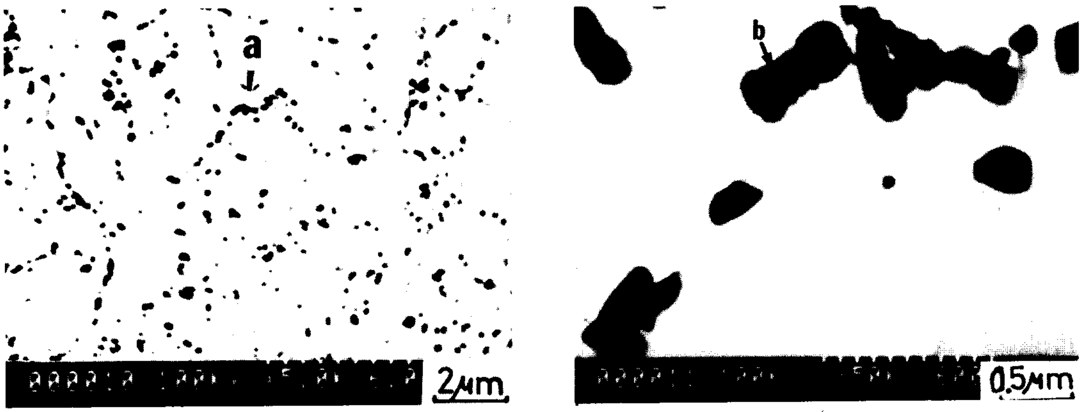
(a) (b)

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



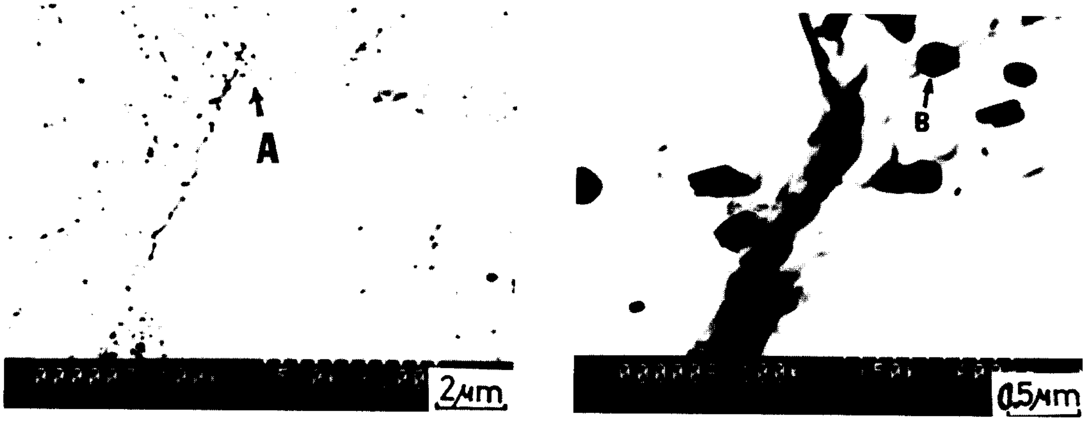
(a) (b)

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



(a) (b)

Photo. 7 Scanning Transmssion Electron Micrographs of Base Metal near HAZ is 9Cr-1Mo Steel weldmet, Normalized, PWHT 730℃×1hr, Angle-cut section.



(a) (b)

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

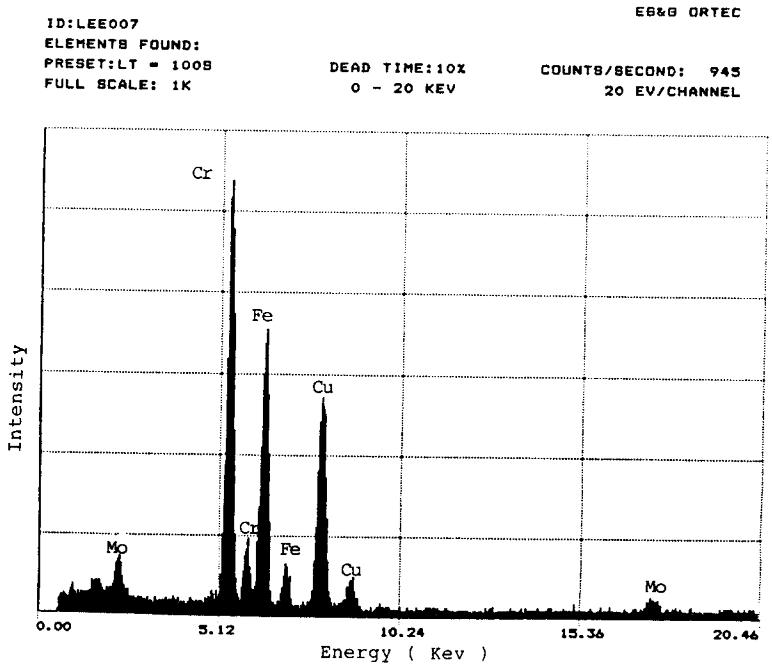


Fig. 8 STEM Micro-analysis of using this film appoximation of the location b in Photo. 7(b)

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

Comparison of these conditions with the tempering study of the same heat[16], reveals that minimum hardness in the HAZ of the weldment that was not tempered after welding, 175 Hv, is approximately 25 Hv points below than produced by tempering at the Ac_1, 810℃ 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-

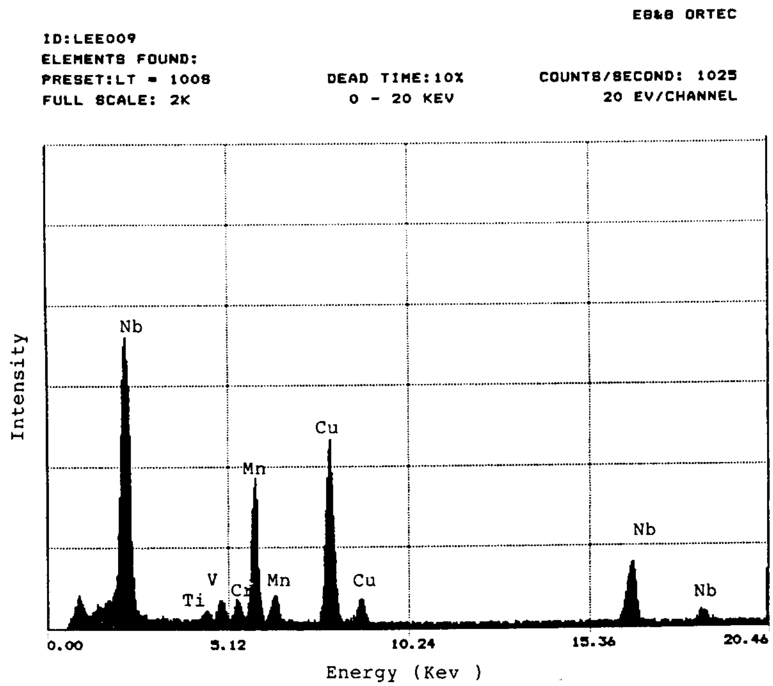


Fig. 9 STEM Micro-analysis of using this film appoximation of the location B in Photo. 8(b)

mately 800℃ for 1 hour.

The slight softening in the affected zone, adjacent to the transformed zone, of 9Cr-1Mo Steel is belived 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 size[17]. 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 conition, the hardness of soft region was 170~200 Hv and is lower than that of the base metal hoth 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 condtion 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 precipition of carbide along the grain and subgrain boundaries.

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

Acknowlegemets

The author gratefully acknowlege the support(1988－1990) from KOSEF(Korea Science and Engineering Foundation), Republic of Korea.

References

1) Pattriaca, P, Hoffman, E. and Cunningham, G : Ferritic steels as Alternate Structural Mateials for High Temperature Applications, P. Patriaca(ed.), Modified 9Cr-1Mo Steel Technical Program Transfer Data Package for Use in Design Analysis, ORNL Laboratory, Oak Ridge, TN, (1982), pp.11－17

2) Sikka, V. : National Program Plan for Commercialization of modified 9Cr-1Mo Alloys, ORNL, Oak Ridge, TN, (1980)

3) Swindeman, R., Thomas, R., Nanstad, R. and Long, C. : Assessment of the Need for an Advanced Chromium-Molybdenum Steel for Construction of Third Generation Gassfier Pressure Vessels, ORNL, Oak Ridge, TN, (1980)

4) Ishiguro, T., Ohnishi, K., Murakami, Y., and Watanabe, J. : Development of a 3Cr-1Mo-1/4V-Ti-B Prssure Vessel steel for the Enhanced Design Stress, R. A, Swift(ed.), Research on Cr-Mo Steels, A SME, Newyork, (1984), pp.43－53

5) Tagawa, H., and Tsyyama, S. : Modified 3Cr-1Mo Steel with Improved Toughness and Elevated Temperature Strength, Compliation of Recent Technical Information for the Program-Materials for Service with Hydrogen at High Temperatures and Pressures, Metals Property Council, Newyork, (1983), pp.15－26

6) Klueh, R. L. and Nasreldin, A. M. : Microstructure and Mechanical Properties of a 3Cr-1.5Mo Steel, ORNL, Oak Ridge, TN, (1985)

7) Eassterling, K. : Intriduction to the Physical Metallurgy of Welding, Butterworths, Boston, (1983)

8) Progrebnoe, N., Tanako, I., and Zozulya, V. : The Effect of Heat Treatment on the Properties of the Softened Zone in Steel 15Kh1MF, Welding Production, 2693, (1979), pp.27－30

9) Challenger, K., Brucker, R., Elger, W., Aand Sovek, M. : Microstructure-Thermal History Correlations for HY-130 Thick Section Weldment, W. Journal, 63(8), (1984), pp.254s－262s

10) King, J. : Weldability, Advanced Alloy Technology Program-Welding Development, ORNL/MSP/1.7－8 1/3－June, (1982)

11) Biss, V. : Metallorgraphic Investigation of Soft regions Near heat affected zones of modified 9 Cr-1Mo, HT-9, and 2 1/4 Cr-1Mo steel weldments, Climax Molybdenum Company Report, J－4747 to ORNL, March, (1982)

12) Vitek, J. M. and Klueh, R. H. : Precipitation Reactions During the Heat Treatment of Ferritic Steels, Metallurgical Transactions, 14A(6), (1983), pp. 1047－1055

13) Sikka, V. : Personal Communication, 2/14/(1985)

14) Seal, A. K. and Honeycombe, R. W. K. : Carbide Precipitati on in Several Steels containing Chromium and Vanadium, Journal of the Iron and Steel Institute, Jan, Vol.44 (1958), pp.9－15

15) Christian, J. : The Theory of Transformation in Metals and Alloys, PP. 691－696, Pergammon Press

16) T. Wata : The Continuous Colling Transformation Diagram and Tempering Respones of 9Cr-1Mo-V-Nb steels, Climax Report J－4672, July, (1981)

17) C. D. Lundin, M. W. Richey, J. A. Henning : Transformation, Metallurgical Response and Behavior of the Weld Fusion Zone and Heat Affected zone in Cr-Mo Steels for Fossil Energy Application, ORNL, sub/81－7685/01&77. (1984)