ATOM PROBE MICROANALYSIS OF WELD METAL IN A SUBMERGED ARC WELDED CHROMIUM-MOLYBDENUM STEEL

B. Josefsson, A. Kvist, H. Andrén

JOURNAL DE PHYSIQUE
Colloque C6, supplément au n°11, Tome 48, novembre 1987

ATOM PROBE MICROANALYSIS OF WELD METAL IN A SUBMERGED ARC WELDED CHROMIUM-MOLYBDENUM STEEL

B. Josefsson, A. Kvist and H.O. Andrén

Department of Physics, Chalmers University of Technology,
S-412 96 Göteborg, Sweden

Résumé - Un acier 2.25Cr - 1Mo, soudé sous flux, est été étudié par microscopie électronique, microscopie ionique à émission de champ et la sonde à atomes. La microstructure bainite de l'acier soudé consiste en ferrite et martensite. En traitment thermique à 690°C martensite se transforme en ferrite et cémentite, et carbures $(Cr,Mo)_2C$ en forme d'aiguille se forment. Avec une réduction de la densité de dislocations, cela a resulté d'une amélioration de la tenacité de l'acier.

Abstract - A submerged arc welded 2.25Cr - 1Mo steel has been investigated using electron microscopy and atom probe field ion microscopy. The bainitic microstructure of the as-welded steel consisted of ferrite and martensite. During heat treatment at 690°C the martensite transformed to ferrite and cementite and needle-shaped $(Cr,Mo)_2C$ carbides precipitated. Together with a substantial decrease in dislocation density, this resulted in an improvement of the toughness.

I - INTRODUCTION

Since the 1930's, chromium-molybdenum steels have been used in the fabrication of pressure vessels and boiler steam tubes. A steel of composition 2.25Cr - 1Mo - 0.1C was originally designed for use at elevated temperatures where creep resistance is required. More recently this steel has also been used in the off-shore oil industry because of its resistance to sulfide induced stress corrosion cracking. Submerged arc welding is often used when fabricating large size components of this type of steel. However, this high heat input welding method sometimes produces welds with low impact strengths. A study of the microstructure of weld metal in both the as-welded state and after a commercially used post-weld heat treatment of 1 hour at 690°C was therefore performed in an attempt to better understand the reasons for this behaviour.

II - EXPERIMENTAL

The heat input during submerged arc welding into the weld was ~ 3 kJ/mm. A cross-section of the multi-run welded 20 mm plates is shown in Fig. 1. Analysis by optical emission-spectrometry of the weld is given in Table I. The as-welded material and also part of the material, which had been heat treated for 1 h at 690°C, were tensile tested and tested for impact strength. The microstructure was characterised using optical microscopy, transmission electron microscopy (TEM) and field ion microscopy (FIM). Local chemical compositions were determined by atom probe (AP) analysis. Specimens for TEM, FIM and AP were taken from the last welded run, because underlying layers had been influenced

by subsequent welding runs. Thin foils for TEM were electropolished in a 10% perchloric acid solution in glycerol and ethanol at room temperature using a Struers Tenupol. The floating layer technique was used to prepare specimens for FIM and AP analysis in a 5% perchloric acid-glycerol-ethanol solution. In the final specimen preparation step, material was removed in a controled manner by stepwise elctropolishing and subsequent examination by TEM until a volume of interest was in a suitable position for analysis. The atom probe used in this investigation has been described previously [1,2]. Before each analysis the specimen was imaged using neon as imaging gas. All analysis were made at 80 K.

III - RESULTS

Mechanical Properties. Results of tensile- and Charpy-V testing are given in Fig. 2. A decrease in tensile strength after heat treatment is evident. The ductile-brittle transition temperature for the as-welded material was above +20°C while the transition temperature for heat treated material was somewhat better, ~ -10°C. The brittle fractures were transcrystalline.

Microstructure. Optical microscopy combined with TEM showed that the microstructure, in both cases, could be described as bainitic. A bright field TEM image of the as-welded material is shown in Fig. 3. The dark areas with sharp contours are martensite and the rest is ferrite. (The dark contrast is probably due to a greater thickness of the martensite areas because of a somewhat lower electropolishing rate.) The size of the ferrite grains was ~ 10 µm and the dislocation density was very high. An atom probe mass spectrum recorded in the ferrite is shown in Fig. 4, and the corresponding composition is given in Table II. A very low concentration of carbon, 0.005±0.003 wt%, was present in the ferrite.

After heat treatment the martensite had transformed to cementite and ferrite and the dislocation density of the ferrite decreased. Some precipitates were observed by TEM, and identified by energy dispersive X-ray analysis (EDX) as being of the $M_{23}C_6$-type [3], Fig. 5. Smaller (100 nm) needle-shaped carbides had also precipitated, Fig. 6. Diffraction rings from carbon extraction replicas showed that these precipitates had hexagonal structure with lattice parameters, a = 2.92 Å and c = 4.70 Å, [4]. Atom probe analysis of three precipitates showed that they had the following stoichiometry:

precipitate	1	$(Cr_{0,25\pm0,06}\,Mo_{0,75})_2(C_{0,96\pm0,04}\,N_{0,04})_{0,94\pm0,05}$
	2	$(Cr_{0,49\pm0,04}\,Mo_{0,51})_2(C_{0,94\pm0,03}\,N_{0,06})_{1,08\pm0,03}$
	3	$(Cr_{0,37\pm0,06}\,Mo_{0,63})_2C_{0,93\pm0,05}$

In these analysis, mass to charge (m/q) equals 14 has been interpreted as N^+ rather than Si^{2+}, since the solubility of silicon in M_2C is very low [5]. Field ion micrographs of martensite and M_2C-precipitates are shown in Fig. 7.

IV - DISCUSSION

In order to find the reason behind the poor impact strength of the as-welded material, its microstructure was compared to that of the heat treated material. One reason for the higher tensile strength and the lower impact strength in the as-welded material is obviously the higher density of dislocations. Another difference that could be seen in the microstructure is that the martensite in the as-welded condition is replaced by cementite, M_2C and some $M_{23}C_6$ precipitates in the heat treated material. The low carbon content of the ferrite in the as-welded condition and the rather low volume fraction of martensite suggest that the martensite has a high carbon content and therefore is hard and brittle. Obviously the high carbon martensite is more detrimental to the toughness than cementite and some $M_{23}C_6$ precipitates. The M_2C precipitates are probably too large to be efficient obstacles for dislocations, and therefore do not affect the toughness very much.

Absorption of nitrogen is often a problem in welding. Nitrogen absorption may e.g. lead to the formation of small nitride precipitates which may induce a lower toughness. The atom probe analyses show that in the present case this can be excluded, since the nitrogen concentration was low in the rather large M_2C precipitates.

In both cases the microstructure could be described as bainitic. A possible mechanism for the formation of high carbon martensite could be, that the austenite-bainite transformation resulted in the formation of bainitic ferrite laths and the carbon diffused ahead of the transformation front. When the carbon concentration ahead of the front became too high, the growth of ferrite stopped resulting in an area of retained austenite. Due to the high cooling rate, about 8°C/s in the range 800-500°C [6], the retained austenite then transformed to high carbon martensite.

V - CONCLUSION

1. The microstructure of both as-welded and heat treated 2.25Cr - 1.0Mo - 0.1C steel is bainitic.
2. The as-welded microstructure contains ferrite of a high density of dislocations and areas of martensite of probably high carbon content.
3. The heat treated steel contains ferrite, cementite and small needle-shaped M_2C precipitates with average composition:
$$(Cr_{0.41\pm0.03}Mo_{0.59})_2(C_{0.96\pm0.02}N_{0.04})_{1.02\pm0.02}$$
4. In the heat treated material, also some $M_{23}C_6$ precipitates were observed.
5. The decrease in tensile strength and the decrease in ductile-brittle transition temperature, which is brought about by heat treatment, is probably due to a decrease in dislocation density and the absence of hard, brittle martensite.

References

[1] H.O. Andrén and H. Nordén, Scand. J. Metall. 8 (1979) 147.

[2] H.O. Andrén, J. Physique 47 (1986) C7-483.

[3] Todd J A, Scripta Metallurgica, 20 (1986) 269.

[4] Andrews K W, Dyson D J and Keown S R, "Interpretation of Electron Diffraction Patterns", Adam Hilger Ltd, London 1971.

[5] Landolt-Börnstein, "Structure Data of Elements and Intermetallic Phases" Springer-Verlag, Berlin 1971.

[6] Easterling K, "Introduction to the Physical Metallurgy of Welding" Butterworths & Company Ltd, 1983.

C	Cr	Mo	Mn	Si	Cu	Ni	O	N
0.08	2.26	0.89	0.61	0.15	0.12	0.05 wt%	271	99 ppm

Table I. Composition of the weld by optical emission spectrometry.

C	Si+N	O	Cr	Mn
0.005±0.003	0.20±0.04	0.005±0.003	2.43±0.12	0.72±0.07
Fe	Mo	Cu	Ni	
95.54±0.17	0.98±0.08	0.08±0.02	0.04±0.02	

Table II. Composition of the ferrite in the as-welded material derived from an atom probe analysis.

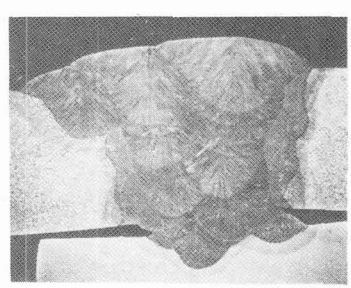

Fig. 1. *Optical micrograph showing a cross section of the weld. The plates are 20 mm thick and were welded in 9 runs.*

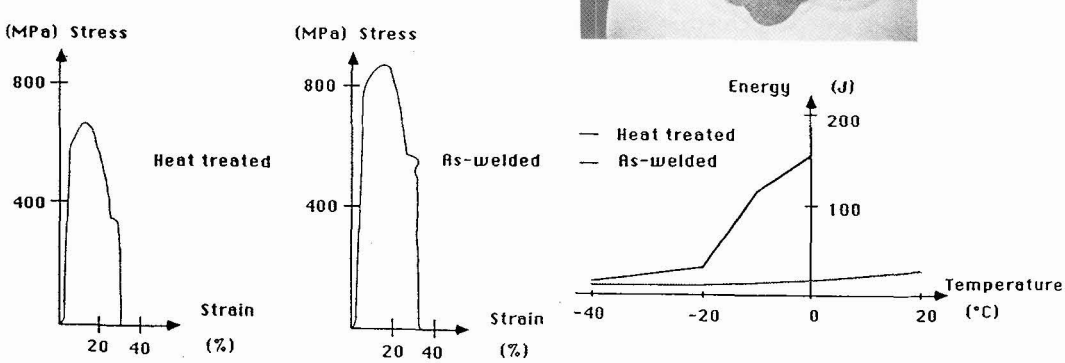

Fig. 2 *Results of tensile strength- and Charpy V testing. (For each tested temperature 5 samples were used.)*

Fig. 3. *Bright field TEM image of the as-welded material. The dark areas with sharp contours are martensite and the rest is ferrite.*

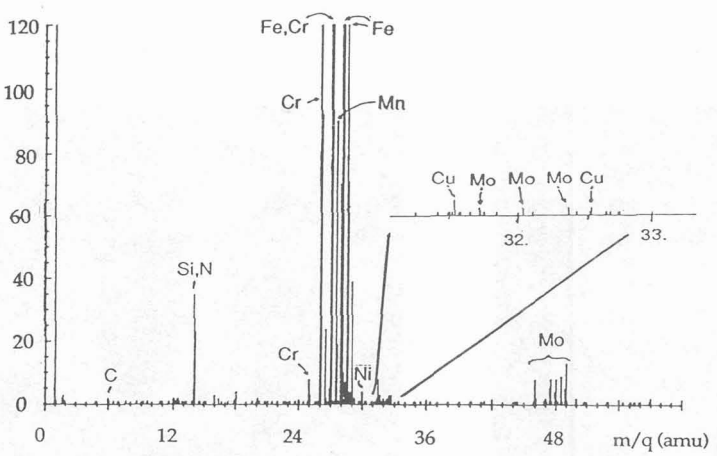

Fig. 4. *Atom probe mass spectrum of ferrite in the as-welded material.*

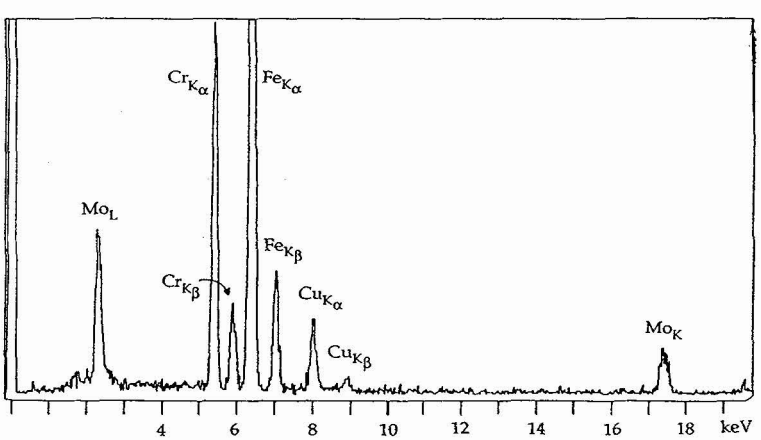

Fig. 5. *EDX-spectrum of $M_{23}C_6$ in the heat treated material. The metal content was about 58 wt% Fe, 22 wt% Cr and 17 wt% Mo. (The copper signal comes from the specimen holder.)*

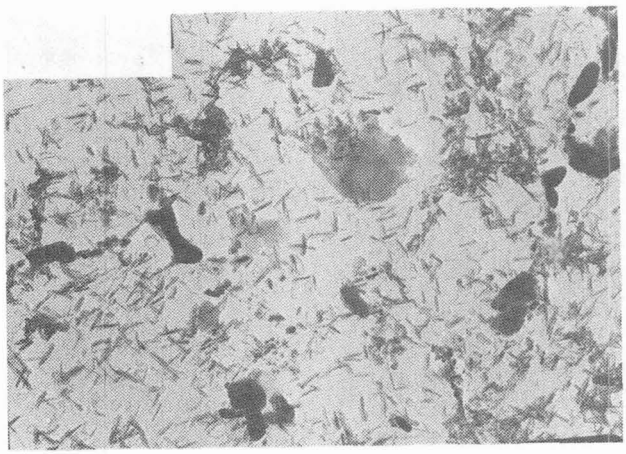

Fig. 6. *Carbon extraction replica of the heat treated material. The needle-shaped particles are of M_2C-type and most of the dark areas are cementite. Some of the dark areas were found to be $M_{23}C_6$ particles by EDX-analysis.*

1 µm

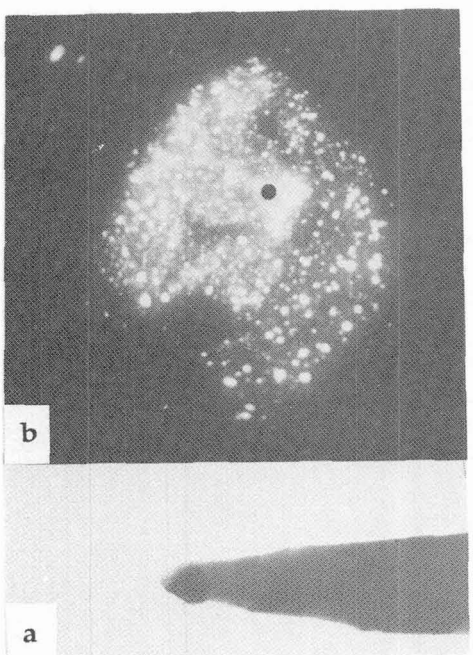

Fig. 7a. *Bright field TEM micrograph of the as-welded material. The dark area at the tip is martensite. At the tip apex there is a thin layer of ferrite.*
Fig. 7b. *FIM image of the same specimen after field evaporation. The brighter area to the left is ferrite, and the darker, more irregular area to the right is martensite.*

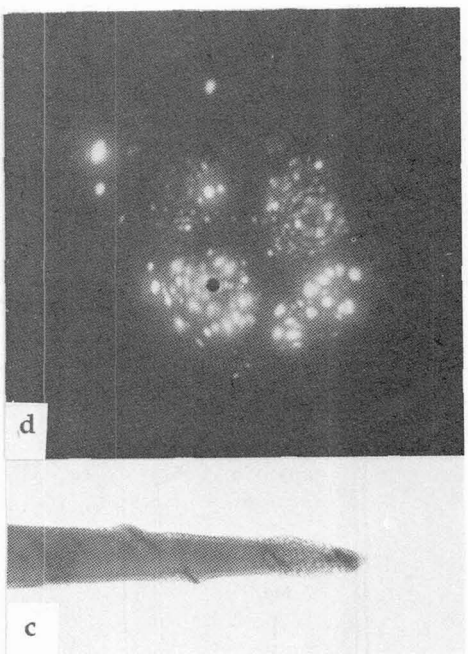

Fig. 7c. *Bright field TEM micrograph of the specimen after heat treatment. M_2C precipitates can be seen.*
Fig. 7d. *FIM image of the same specimen. Lower part shows precipitates and the position of the aperture of the first analysis.*