Behaviour of Precipitates in Bond Region of Overlay Welding (Report I)†

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Abstract

Structure and behaviour of carbides precipitated to bond region of stainless steel overlay weld with submerged arc welding was studied. Observations by optical and electron microscopes, electron diffraction, and state analysis of the extracted residues by X-ray diffraction were used. It was determined that carbide precipitated in the boundary between austenite and ferrite had fcc structure and lattice spacing of a_0 = 10.80Å and it was considered to $M_{23}C_6$ although distinct conclusion was not given by X-ray diffraction. In order to know distribution of various elements in weld, analysis by ion microanalyzer (IMA) was applied.

1. Introduction

In general, band arc welding is widely used to overlay method of steels for the chemical industry use because it is specially required good corrosion resistance and it has the following benefits.[1]

1) It has high deposition efficiency.
2) Depth of penetration is shallow.
3) Wide bead is obtained by one-pass.
4) In spite of simple instrument, good weldability is obtained.
5) Consumption of flux is low.

On the other hand, the following conditions is necessary to overlay welding of austenitic stainless steel.[2]

1) No defects such as weld crack do occur.
2) Weld metal must have good corrosion resistance.
3) Weld must have good mechanical properties.
4) No remarkable change of properties occurs by heat treatment.

When weld is put onto austenitic stainless steel, two phase structures having several percentages ferrite is recommended to prevent hot cracking. Usually, stainless steel weld must be heat-treated for the following reason, softening of work hardening, improvement of corrosion resistance, decomposition or dissolution of carbides and sigma phase precipitated from hot-working. From the request of heat treatment to release residual stress induced from welding, the problem of stress relief emblittlement was frequently introduced. It has been established that the cause is attributed not only to the diffusing behaviour of carbon atom, but also to carbides precipitated at grain boundaries.

Until now, the structure of carbides, composed of chromium, molybdenum and other elements, have been summarized in detail.[3),4)] Further, the constitution, the morphology and the location to precipitate were elaborately studied.[5)]

In the field of iron- and steel-making, state analysis to do systematized chemical analysis was built on.

In Table 1, it is shown that two sorts of chromium carbides, Cr_7C_3 or $Cr_{23}C_6$, are stable forms. Chromium carbides can dissolve iron, or dissolves to matrix. Molybdenum forms MoC, Mo_2C or complex carbide as M_aC_b. Molybdenum can dissove to matrix. The space lattice and lattice dimention are given in Table 2.

In this report, identification of carbides precipitated at the boundaries between stainless steel and base metal

Table 1 Carbindes in the system Fe-Cr-C[4)]

Carbide	Space Lattice	Lattice Dimensions
Fe_3C	Orthorhombic	a = 4.514 Å b = 5.079 c = 6.730
$Cr_{23}C_6$	Cubic, face-centred	a = 10.64
Cr_7C_3	Trigonal	a = 13.98 c = 4.523
Cr_3C_2	Orthorhombic	a = 2.821 b = 5.52 c = 11.46

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Table 2 Carbides in the system Fe-Mo-C[4]

Carbide	Space Lattice	Lattice Dimensions
Fe_3C	See Table 1	
MoC	Hexagonal	a = 2.898 Å c = 2.809
Mo_2C	Hexagonal	a = 3.022 c = 4.724
$M_{23}C_6$	Cubic, face-centred	a = 10.52
M_6C	Cubic, face-centred	a = 11.08
M_aC_b	Unknown	

was carried out as first step of the study of overlaid welding. Specimen used is stainless steel overlay weld on the corrosion resistant alloying steel with submerged arc welding. Precipitates were extracted with acid or electrochemical mean, and they were examined with several methods such as X-ray diffraction analysis by Debye-Scherrer mean, observation by optical and electron microscopes, and electron diffraction.

2. Experimental specimens

Chemical compositions of base metal and band electrode are given in Table 3. In this study, ASTM 533B as base metal was one layer overlaid. 309 steel was used as hoop, and flux is composed of the system $CaO-Al_2O_3-MgO-CaF_2$.

Table 4 Welding condition

Arc Current	Arc Voltage	Welding Velocity	Electrode Length	Pre-heating
1200A (D.C. R.P.)	27 V	18 cm/min.	45 mm	150 °C

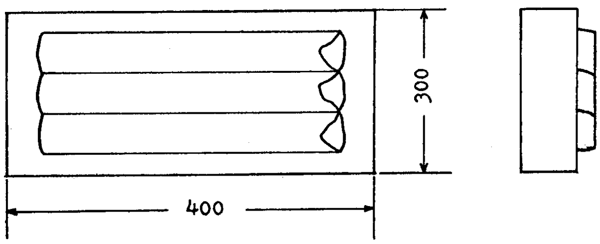


Fig. 1 The overlaying size

Table 5 Chemical compositions of weld metal (wt%)

	C	Cr	Ni	Mo
stainless 1	0.050	18.73	10.78	0.096
bond 2	0.331	Tr.	0.72	0.534

Table 3 Chemical compositions of base metal

		Elements (wt%)							
		C	Si	Mn	P	S	Ni	Cr	Mo
base metal	t mm 40 x 300 x 400	0.19	0.26	1.32	0.010	0.005	0.60	–	0.51
wire	mm 0.4 x 75	0.021	0.35	1.82	0.021	0.017	11.20	22.11	0.24
flux	mesh 12 x 100	$CaO-Al_2O_3-MgO-CaF_2$							

In Table 4, welding conditions such as arc current, voltage, preheating, welding speed, electrode length, preheating path interval, and temperature are given.

In Fig. 1, the overlaying size is shown. Restraint was carried out with SM41B having 25 width x 100 mm height, and welded to be a well crib. As arc current, DCRP was employed.

In Table 5, chemical composition of weld metal is given.

Specimens for microscopical observation and extraction were cut and cleaned with acetone and alcohol, after buff-polished, and continuously dried. Further, chiplike specimen was prepared for extraction with acid. Specimens for electron microscopical observation were treated with the following processes:

Specimen from stainless steel side was cut to be about 0.3 mm thickness and reduced to be 0.15 mm with mechanical polishing. Afterwards, it was etched with phosphoric acid-chromic acid combination. (Window method)

Specimen from base metal was reduced to be 50μ thickness, and the portion was etched with needle method. Both specimens were as weld.

On the other hand, specimen was heat-treated at

1100°C for 2 hr and water-quenched and continuously stress-released at 650°C for 20 hr is now in progress.

Studies of the specimens, as weld and SR treated are now proceeding with IMA (ion microanalyzer).

3. Experimental methods

Extraction with acid as well as electrochemical means were performed in conical flask shown in Fig. 2.

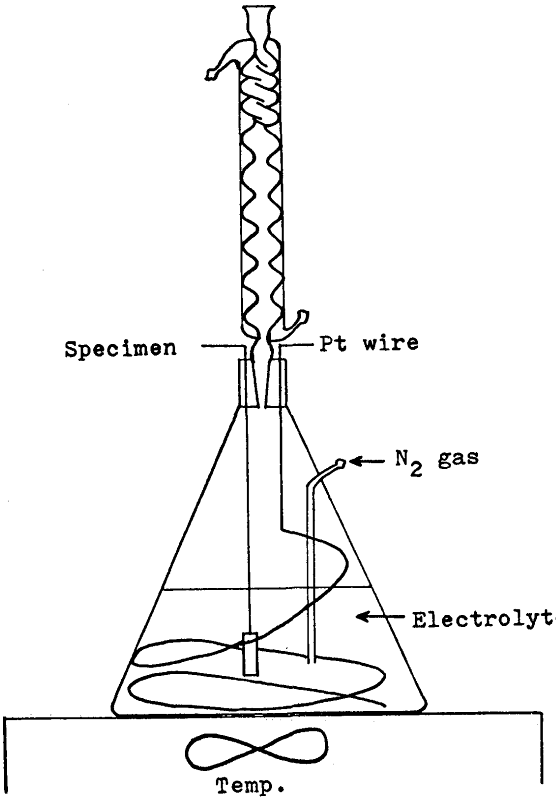


Fig. 2 Conical frask type

In the latter case, specimen was hung and surrounded with platinum electrode. Magnetic stirrer was used for agitating electrolyte, and atmosphere in flask was maintained with nitrogen to prevent oxidation.

As other means, extracting vessel named Koch-Sundermann type and vessel connected to potentiostat were used together. These apparatuses are shown in Figs. 3 and 4.

Extracted residues were separated with a centrifuge, and dried in vaccum dryer after washed. Recovery of residues was acted with the uses of filter with suction and sieve with ultrasonic wave.

Extracted residues were identified with X-ray diffractometer (Rigaku-Denki Co. type D-3F).

Electron microscopical observation and electron diffraction were performed under the accelerated voltage of 200KV (JEM, 200 type), and the selected area electron diffraction was used to identify crystal structure of specimen.

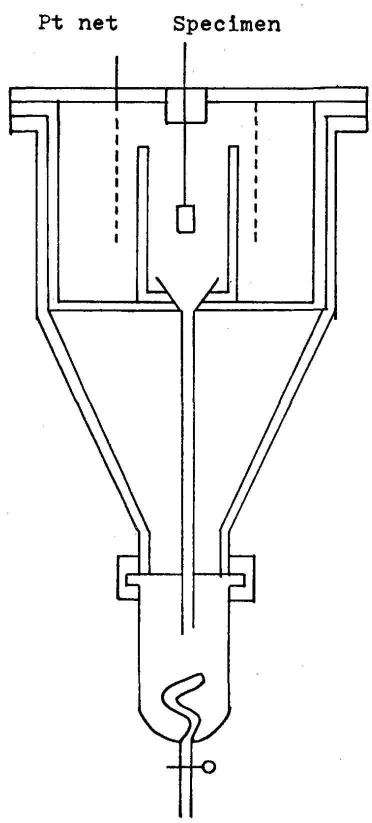


Fig. 3 Koch-Sundermann type

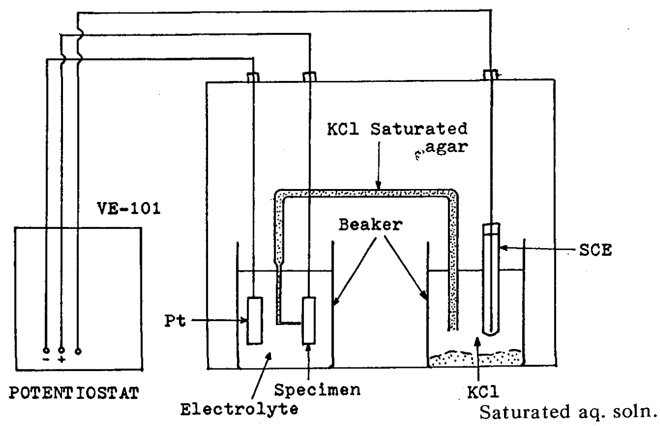


Fig. 4 Circuit diagram of apparatus

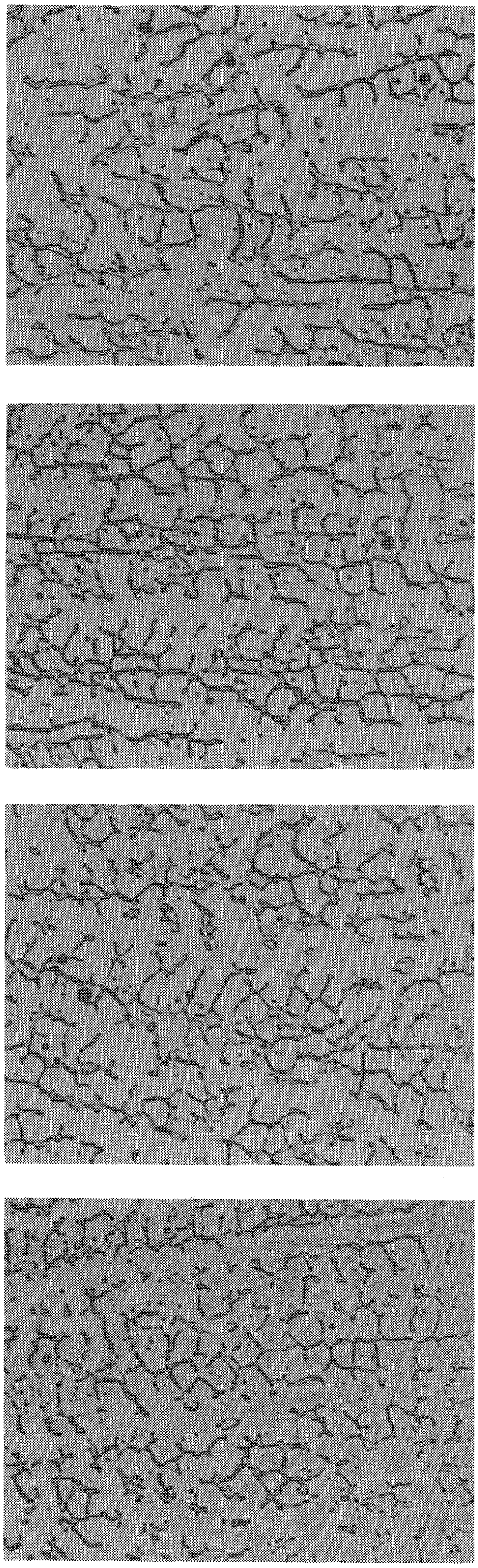
4. Examination of extracting conditions

Many report concerning state analysis of carbides (chromium and molybdenum) formed in steel were presented until now. In this study, the authors referred various proposals such as the use of NaCl-EDTA neutral electrolyte,[6),9)] application of H_2SO_4,[10),11)] potentiostatic extraction with citric acid[12)], the use of 30N-H_3PO_4[13)], and the employment of H_3PO_4 (2+1)[14)]. Also, potentiostatic extraction of various compounds was referred.[15)]

5. Experimental results and discussion

According to Scheffler's diagram, (Fig. 5), it is thought that sample used in this study is composed of several percentages ferrite and austenite. In Phote. 1, it was understood that this estimate was correct.

In Photo. 2, metallographic texture of base metal is shown. At the position appart 1 mm from boundary, a lot of cementite was observed. Results by electron microscopy are shown in Photos. 3 and 4. From the selected area electron diffraction analysis, it was determined that ferrite had bcc structure and the lattice parameter of $a_0 = 2.87\text{Å}$ and austenite as base metal showed fcc structure having lattice parameter of



1mm

2mm

3mm

4mm

x 300

Photo. 1 Stainless side (x300)

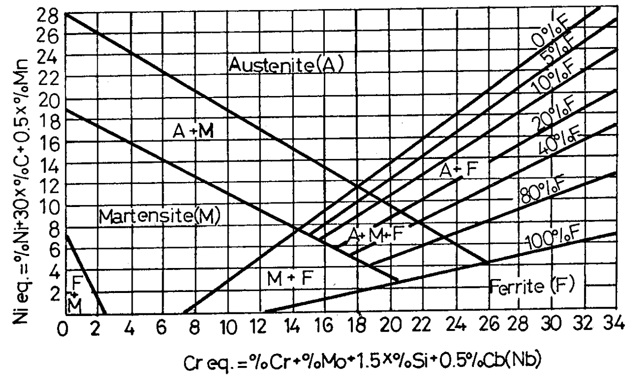


Fig. 5 Schaeffler's diagram

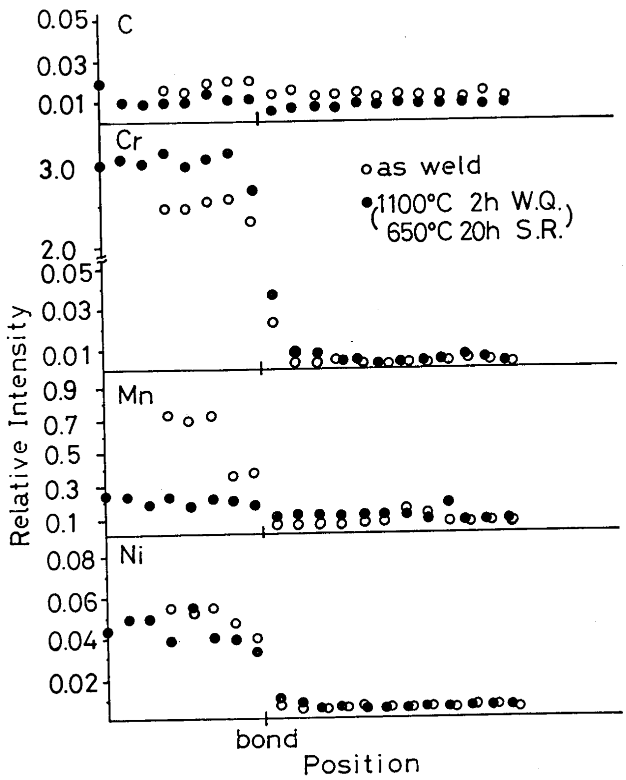


Fig. 6 Distributions of various elements in weld metal

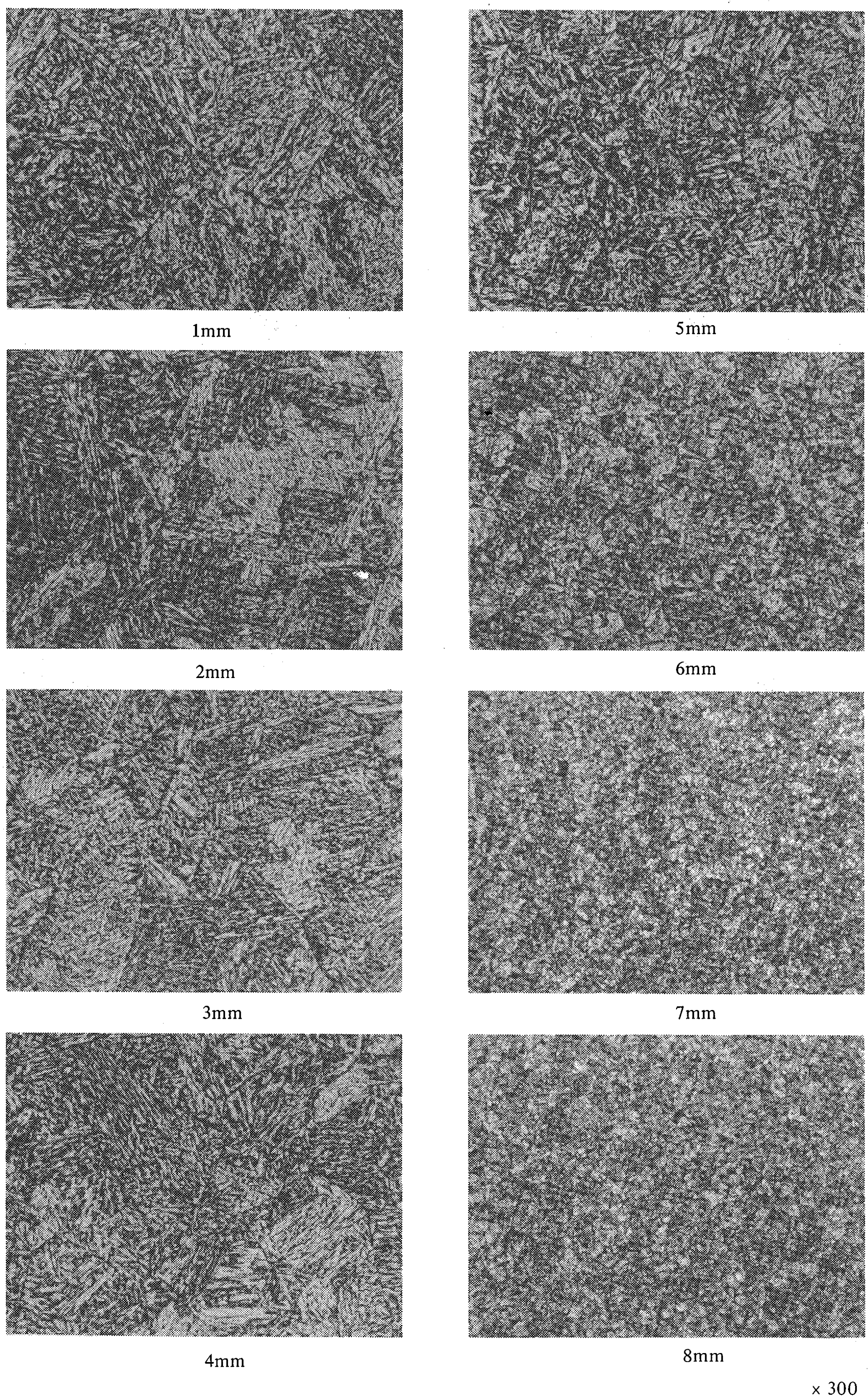


Photo. 2 Side of base metal (x 300)

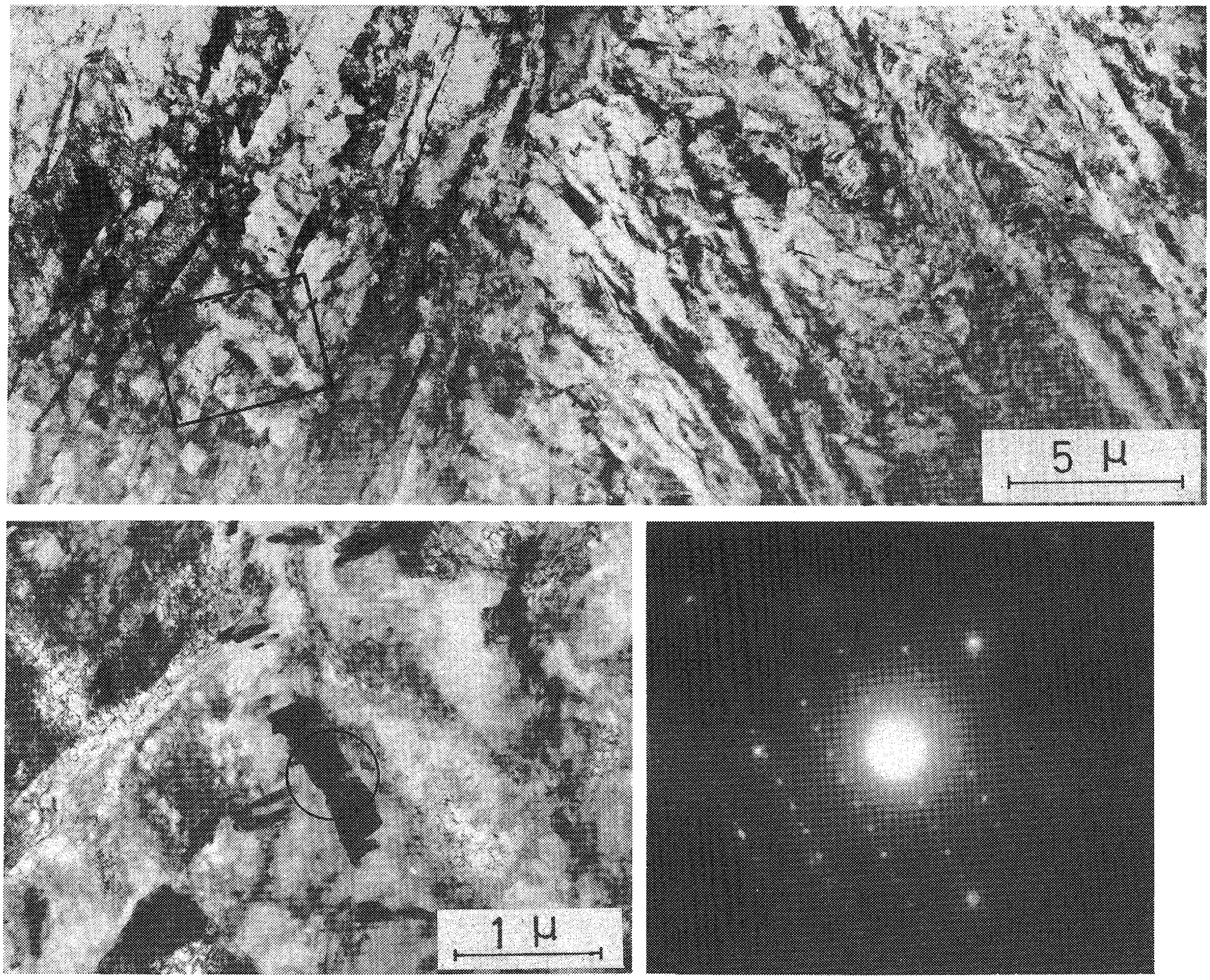
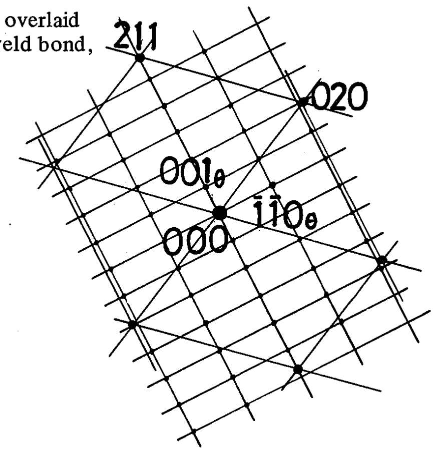


Photo 3. Transmission electron micrograph of sub-structure in overlaid mild steel taken from the part apart 1mm from the weld bond, showing fine cementite precipitates and ferrite.



$a_o = 3.60\,\mathring{A}$.

Carbide precipitated at boundaries between austenite and ferrite showed fcc structure having lattice parameter of $a_o = 10.80\,\mathring{A}$. As shown in table 1 and 2, $M_{23}C_6$ and M_6C take fcc structure. Carbide observed in this study was considered to $M_{23}C_6$ from the result by X-ray analysis.

Further, lameller cementite and ferrite were observed in the base metal from electron microscopical observation and electron diffraction result.

In Fig. 6, the result obtained by IMA is shown as an example. It seems effective method to determine the distribution of minor elements such as chromium and carbon atoms.

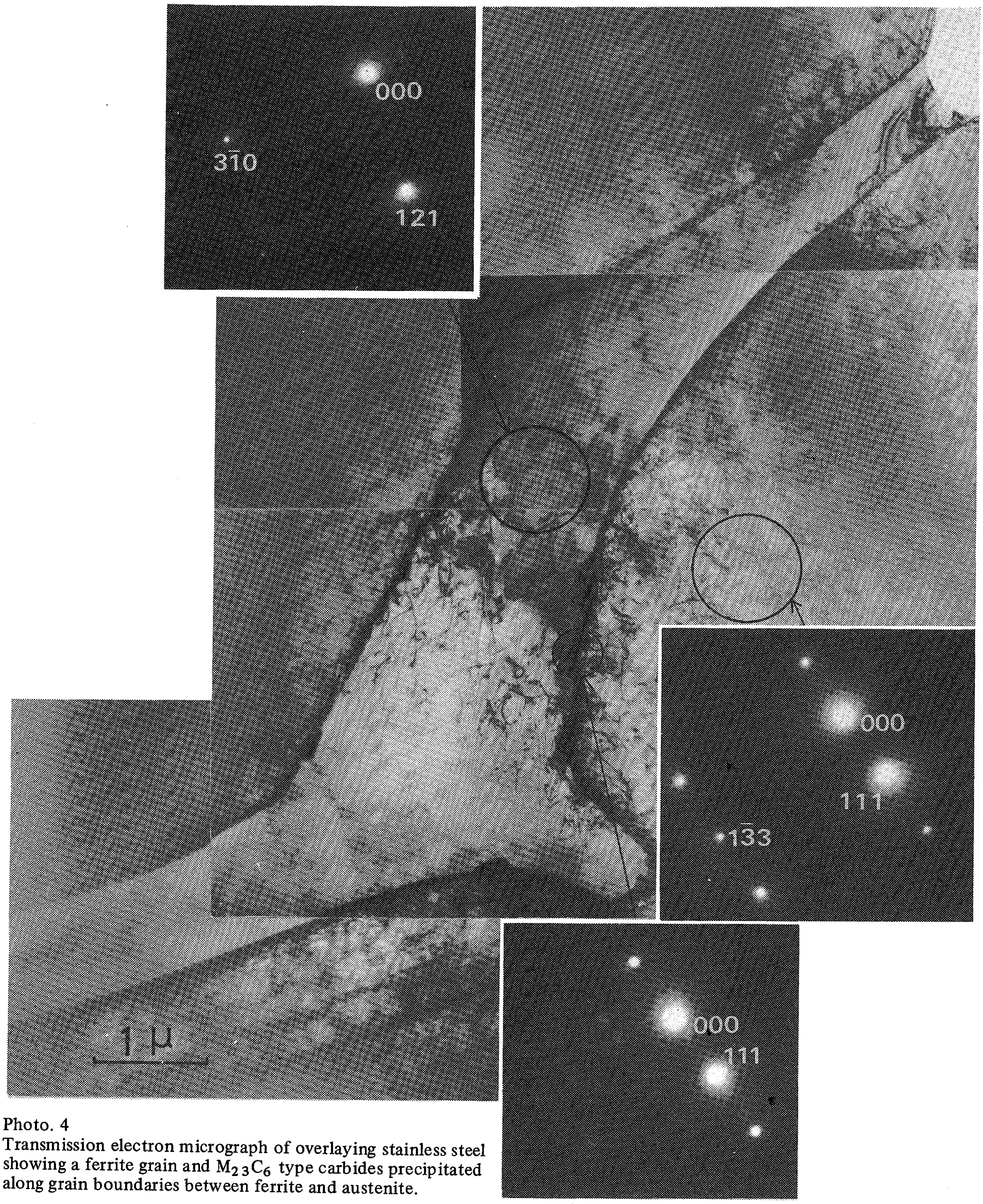


Photo. 4
Transmission electron micrograph of overlaying stainless steel showing a ferrite grain and $M_{23}C_6$ type carbides precipitated along grain boundaries between ferrite and austenite.

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