Fine Oxide Particles in Mild Steel CO_2 Weld Metal

Fine oxide particles are genuine features of carbon extraction replicas of mild steel CO_2 weld metal. These small particles are distinct from the usual non-metallic inclusions which are several orders of magnitude larger in size

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ABSTRACT. Fine oxide particles, 50-600 Å (0.005-0.06 μm) in diameter, the existence of which has been hitherto disputed, have been found as genuine features on carbon extraction replicas of mild steel CO_2 weld metal. These particles are distinct from the usual non-metallic inclusions which are 0.4-2 μm in diameter. Clear electron diffraction patterns were obtained from the fine oxide particles, and the interplanar spacings computed agreed relatively well with the cubic spinel $MnO \cdot Fe_2O_3$.

Introduction

Irvine and Pickering[1] observed fine precipitates of 100-400 Å (0.01-0.04 μm) diameter in the electron microscope on carbon extraction replicas obtained from basic MMA (manual metal arc) mild steel weld metal. These authors found it difficult to obtain clear electron diffraction patterns which could be readily identified, and they tentatively assumed the precipitates to be Fe_3O_4 spinel. Wheatley and Baker[2] observed similar effects on the replicas but they could not obtain any diffraction patterns at all. In thin foils, perhaps because of the large dislocation density typical of the MMA weld metal, no particles corresponding with the replica effects have been seen.[3] Therefore, it has been concluded[3] that the replicas showed no particles but etching effects, perhaps associated with local microsegregation.

Hrivnak[4] has carried out oxidizing and reducing experiments with various irons and has argued that these experiments show the occurrence of genuine microparticles. He could obtain no diffraction patterns, apparently because the particles were only 20-50 Å (0.002-0.005 μm) thick. He argued that the linear dimension of 200-300 Å (0.02-0.03 μm) taken sometimes for the particle-size is that of an etch pit around the particle.

This note gives observations and electron diffraction data for particles similar to those described by all the previous authors, but found in mild steel weld metal deposited by the CO_2-shielded metal arc process. At this stage it would be convenient to define the microscopic appearance of the various particles found in this and other mild steel weld metals deposited by the various metal arc processes.

In addition to the usual microstructure of ferrite, retained austenite and carbides, the weld metals contain globular *non-metallic inclusions*. These inclusions are best observed under the light microscope on the as-polished microsections. Figure 1 shows such inclusions in the mild steel CO_2 weld metal examined in this work. The majority of these inclusions are 0.4-2 μm in diameter. In this weld metal the globular non-metallic inclusions are glassy manganese silicates.[5] In other metal arc weld metals, non-metallic inclusions can incorporate other metal oxides[6] and the incidence of large inclusions (about 10 μm diameter) can increase with oxygen content.[7]

The *fine particles* considered in this note are quite distinct from the non-metallic inclusions and they cannot be seen in the light microscope. Figure 2 shows an electron micrograph of these

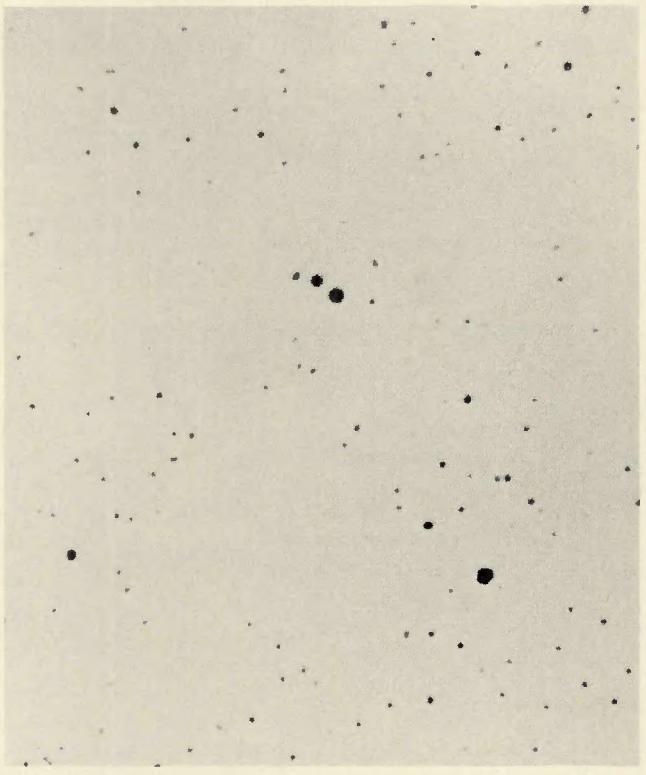

Fig. 1—Non-metallic inclusions in mild steel CO_2 weld metal. As polished; light micrograph; X1000

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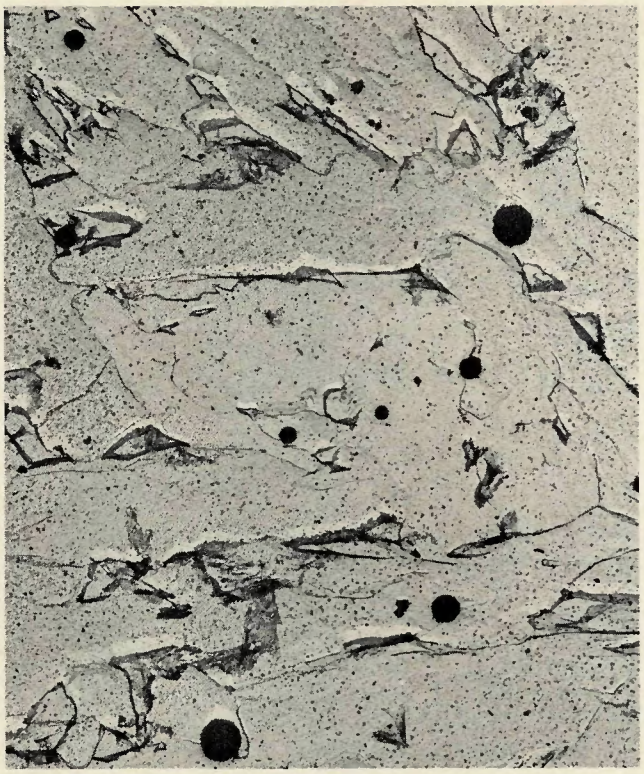


Fig. 2—Fine particles and non-metallic inclusions on carbon extraction replica of mild steel CO_2 weld metal. 2% Nital etch. Electron micrograph; X5000

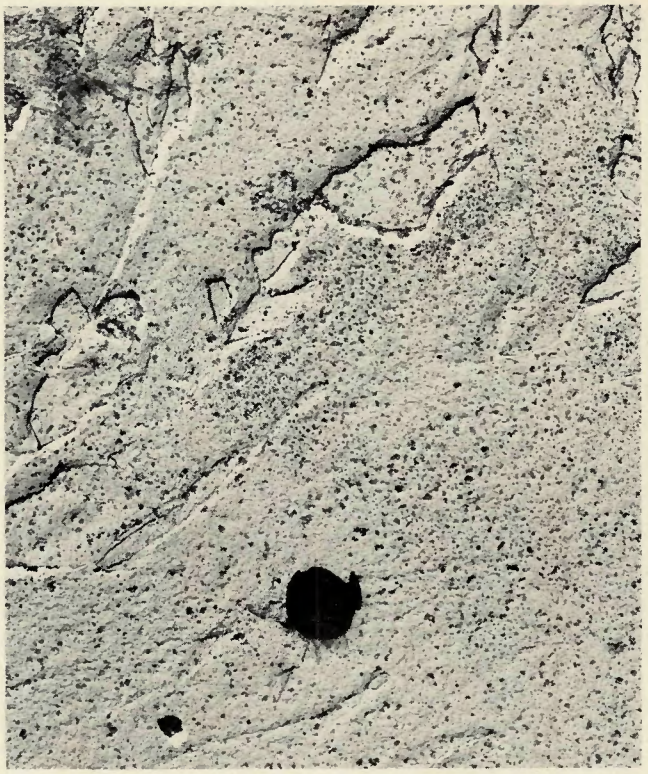


Fig. 3—Area with locally increased density of fine particles on carbon extraction replica of mild steel CO_2 weld metal. Electron micrograph; X7500

Table 1—Chemical Analysis (wt. %) of Materials

Material	C	Mn	Si	S	P	Al (sol)	Ti	Cu	O (ppm)	N
Plate	0.11	0.84	0.25	0.026	0.005	NA	NA	NA	NA	NA
Wire	0.06	1.26	1.08	0.012	0.004	0.016	0.012	0.27	NA	NA
Weld metal	0.08	0.98	0.43	0.017	<0.01	0.008	0.006	0.18	533 580	0.012

NA = not analysed

Table 2—Tensile Properties of All Weld Metal Specimens With $l_o = 5d_o$

Specimen	Tensile properties					
	L.Y.P.		U.T.S.		Elong.	R.A.
no.	N/mm²	ton f/in²	N/mm²	ton f/in²	%	%
1	423	27.4	576	37.3	22.2	57.8
2	423	27.4	579	37.5	24.7	58.4

fine particles in the form of relatively uniformly scattered, background dots on carbon extraction replicas. The black circular features are the same non-metallic inclusions (0.4-1 μm diameter) which appear as small dots under the light microscope (Fig. 1). It can be seen in Fig. 2 that the largest fine paricles are an order of magnitude smaller than the smallest non-metallic inclusions.

Experimentation

The CO_2 weld metal was deposited in 12mm ($^1/_2$ in.) deep 60 deg V-groove cut in 31 mm ($1^1/_2$ in.) thick C-Mn steel plate (Table 1). There were 57 mm ($2\ ^1/_4$ in.) of material on both sides of the groove and the total weld length was about 760 mm ($2^1/_2$ ft). The filler wire, 3.2 mm ($^1/_8$ in.) diameter, contained only Mn and Si (Table 1) as deoxidants. Deposition was done automatically, without preheat, under a current of 660 amp, arc voltage of 35 v and travel speed of 255 mm/min (10 in/min), using a suitably adapted ESAB A6B machine.

The groove was filled flush with the plate surface and the penetration was such that the ratio of the weld metal cross-section to the V-groove cross-section was 2.4/1. The size of the fusion zone enabled all weld metal tensile specimens of $d_o = 7$ mm (0.28 in.) and $l_o = 35$ mm (1.4 in.), to be obtained, the properties of which are given in Table 2.

Microsections were etched in 2% Nital, and carbon replicas were deposited with the specimen surface at 45 deg angle to achieve self-shadowing. The replicas were lifted off by soaking in 2-5% Nital, 2-3 volts being applied sometimes to the specimen (positive) for 10-15 sec if the replicas would not float off within 30 min.

Results

It was found that the fine particles appearing in Fig. 2 gave faint diffraction spots as claimed by Irvine and Pickering,[1] despite the assertions to the contrary by Wheatley and Baker[2] and Hrivnak.[4] These spots were too weak to be seen directly on the electron microscopic screen, but they could be discerned by careful examination of the photographic plates against dimly lit background. To obtain such plates with discernible spots, it was necessary to photograph the diffraction patterns at very low beam intensities, so that the exposure time was in the range 5-7 min. Under the above conditions, the diffuse carbon rings were adequately suppressed and did not mask the weak spots.

It was also noticed after prolonged search that in some areas of the repli-

Table 3—Comparison of Interplanar Spacings Computed From Polycrystalline Diffraction Patterns of Fine Particles With X-ray ASTM Data Cards

	X-Ray ASTM cards								Electron diffraction patterns from fine particles		
	10–319 $MnFe_2O_4$ cubic, spinel		19–629 Fe_3O_4 cubic, spinel		4–0732 $MnO.Mn_2O_3$ cubic, spinel		12–284 Fe_2SiO_4 cubic, spinel				
	a = 8.499 Å		a = 8.396 Å		a = 8.7 Å		a = 8.233 Å				
{hkl}	d, Å*	I/I_1	d, Å*	I/I_1	d, Å*	I/I_1	d, Å*	I/I_1	d, Å	I	a, Å
111	4.91	20	4.85	8	5.10	80	4.75	40			
220	3.01	35	2.97	30	3.09	20	2.91	20	3.04–3.07	W	8.60–8.68
311	2.56	100	2.53	100	2.63	100	2.48	100	2.47–2.48	VS	8.19–8.22
200	2.45	12	2.42	8	2.51	15	2.37	<110			
400	2.12	25	2.10	20	2.17	15	2.05	50	2.15 1.99	S W	8.60 7.96
331	—	—	—	—	—	—	1.89	20	1.89–1.90	VW	8.24–9.28
422	1.73	20	1.72	10	1.77	10	—	—	1.69	W	8.28 8.78
511	1.64	35	1.62	30	1.67	20	1.58	40			
440	1.50	40	1.49	40	1.53	18	1.45	70	1.51	M	8.54
531	1.44	4	1.42	4	—	—	—	—	1.39	VW	8.22 8.89
620	1.34	4	1.33	4	—	—	—	—			
533	1.30	20	1.28	10	—	—	1.26	20	1.29	VM	8.46

* Rounded off to second decimal place

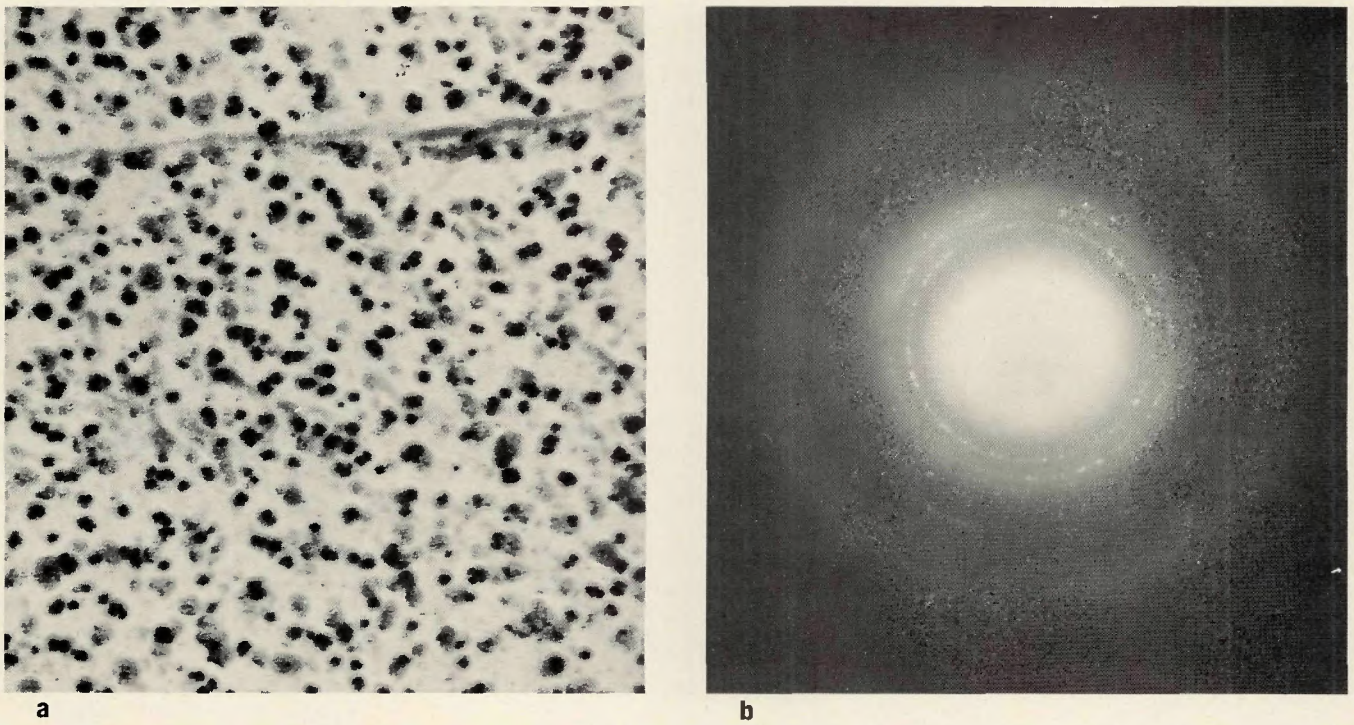
ca, the density of the fine particles was greater than on average (Fig. 3) which was probably due to local microsegregation of some element promoting particle formation. Thus, an opportunity presented itself to obtain polycrystalline diffraction patterns with relatively well developed rings. Figure 4a shows an area from which the diffraction pattern of Fig. 4b was obtained, and the corresponding interplanar spacings are given in Table 3.

These interplanar spacings and their intensities showed relatively good agreement with ASTM X-ray standard of $MnFe_2O_4$. Thus, the present findings are in accord with the tentative identification of such particles as Fe_3O_4 spinel in the MMA weld metal[1] and with the experiments of Hrivnak[4] who ascribed these particles to oxygen in iron and iron alloys. The shape of the fine oxide particles (Fig. 4a) tended to be cubic, which was compatible with the presumed cubic crystal structure (Table 3). The linear size of the particles varied between 50-600 Å.

Some deviation from the ideal $MeO_oMe_2O_3$ structure observed in the diffraction patterns could be ascribed to the interference from cementite, although care was taken to avoid the cementite bearing areas. It is therefore likely that this deviation is a result of the tendency to form the cubic Fe_2SiO_3 silicate, the lattice parameter of which is very similar to those of the $MeO_oMe_2O_3$ spinels (Table 3).

Discussion

While it can be now accepted that fine oxide particles are a genuine feature of steel weld metal microstructure, their role in influencing the various mechanical properties is uncertain. It can be accepted that they have insignificant effect on the yield and tensile strengths in comparison with the effect of grain size[1, 2]. How-



a b

Fig. 4—Electron micrograph showing shape of dense fine particles. (b) electron diffraction pattern of the above area

ever, in the case of notch toughness, when the metal microstructures and compositions are similar, the fine oxide particles may have some effect, by modifying the geometry of dislocation motion and the incidence of pile-up formation.

One ought to expect the fine oxide particles to affect creep rupture behaviour of steel weld metals. There has been some indication that the fine oxide particles can form in 2CrMo submerged arc (SA) weld metal deposited under high SiO_2 (30%) fluxes. Such fluxes give SA weld metals with relatively high* (approaching 0.1%) oxygen contents.[7] Practical experience has shown that 2CrMo SA weld metal deposited under high SiO_2 flux can be susceptible to reheat cracking which is a form of grain boundary creep rupture. The fine oxide particles, with diameters ranging between 50-600 Å (0.005-0.06 μm) may weaken grain boundaries by promoting cavity nucleation. It has been shown theoretically[8] that particles 300 Å (0.03 μm) in diameter can nucleate cavities. Boniszewski and Eaton[9] observed V_4C_3 particles 200-600 Å in diameter within the creep cavities of CrMoV steel and weld metal. In the absence of vanadium, (e.g. in 2CrMo weld metal) the role of the fine oxide particles should not be ignored.

* Low oxygen contents in the weld metal are below 0.05%.

Conclusions

1. Fine oxide particles, of square shape with 50-600 Å (0.005-0.06 μm) edge, were observed on carbon extraction replicas of mild steel CO_2 weld metal. These particles are distinct from the globular non-metallic inclusions which are 0.4-2 μm in diameter.

2. Clear electron diffraction patterns were obtained from the fine oxide particles which were identified as $MnOFe_2O_3$ cubic spinel, possibly mixed with some Fe_2SiO_4 cubic silicate, both of similar lattice parameters.

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WRC Bulletin No. 163 July 1971

"Elastic-Plastic Deformations in Pressure Vessel Heads"

By F. A. Simonen and D. T. Hunter

This publication presents the results of an investigation of the elastic-plastic behavior of pressure vessel heads under internal pressure. The work was sponsored over a two-year period by the Pressure Vessel Research Committee, with the first year being devoted to ellipsoidal heads and the second year to torispherical heads. Battell's computer program, NONLEP, developed for elastic-plastic analysis of thin shells of revolution, was applied to a set of typical head geometries subjected to internal pressure. This program includes effects of large deformations and strain hardening and thus it was possible to predict the additional pressure-carrying capability of heads beyond the collapse pressure predicted by limit analyses. Curves giving details of the numerical results are organized as appendices, with the main body of the publication devoted to discussion of the analyses.

"Summary Report on Plastic Limit Analysis of Hemispherical- and Toriconical-Head Pressure Vessels"

By J. C. Gerdeen and D. N. Hutula

The Subcommittee on Shells of the PVRC has been sponsoring a design study for the purpose of formulating design criteria for pressure vessels operating at temperatures below the creep range. Various design criteria have been considered, including elastic stresses, elastic-plastic stresses, buckling, and plastic collapse (limit analysis).

It was noted that both elastic and plastic analyses had been conducted for torispherical- and ellipsoidal-head vessels. For hemispherical-head vessels, only an elastic analysis had been conducted. It was desirable that a plastic analysis also be conducted for these heads. For toriconical heads, detailed analyses of any kind were lacking. Results of plastic limit analysis for torispherical heads had been applied as an approximation to toriconical heads, but the accuracy of this approximation was questionable.

This report describes the proposed work which now has been completed.

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