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Effect of desulphurization and calcium treatments on the inclusion morphology of 0.4C–Cr–Mo–Ni steel

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Several 0.4C–Cr–Mo–Ni steels with different sulphur and calcium content levels have been studied to determine the effect of desulphurization and calcium treatments on the morphology of non-metallic inclusions in low-alloy steels. The volume fraction and size parameters of the inclusions were determined using optical microscopy. The inclusions were identified by electron probe microanalysis. The volume fraction and mean aspect ratio of a stringy type of inclusion, which consisted predominantly of MnS, was reduced significantly with a decrease in sulphur content through desulphurization. A cluster type of composite inclusion was also decreased with decreasing sulphur content. Calcium treatment of steel with a commercial sulphur level was not very effective for modification of the inclusions, producing two types of cluster composite inclusion. However, the calcium treatment of desulphurized steel modified dramatically the stringy type to a particle type (mean diameter: 1.3 μm) which consisted predominantly of CaS–CaO, while small amounts of Ti and Al were also detected.

1. Introduction

In recent years, commercial structural low-alloy steels have been used in many engineering components in quenched and tempered conditions. Recently, increased use has been made in critical structural applications under severely stressed situations in severe environments. As a result, the steels used for these purposes require better ductility and toughness as well as higher strength in severe conditions. Isotropy regarding these properties is an especially necessary requirement. So far, in order to meet such requirements, many improvements have been made with microstructural control through thermal and thermomechanical treatments [1–12].

Although modification through microstructural control has benefits for dramatically developing the mechanical properties of the steels, it is not very promising for modifying the isotropy of the properties. An effective approach for solving this problem is to modify the morphology of non-metallic inclusions in the steels. In such a case, a better approach taken to modify the inclusion morphology is either to reduce the sulphur content levels of the steels or to modify the inclusion morphology in the steels by chemical means such as addition of alkaline rare-earth metals, e.g. calcium and magnesium, or rare-earth metals, e.g. cerium and lanthanum, to molten steel [13–17].

In the present work, 0.4C–Cr–Mo–Ni steels have been studied to determine the effect of desulphurization and calcium treatments on the inclusion morphology of low-alloy steels.

2. Experimental procedure

Several 0.4C–Cr–Mo–Ni steels with different sulphur and calcium content levels were used in this investigation. The chemical composition and gas analysis of the steels are given in Table I. All the steels were prepared as 10 Mg electric furnace air-melted and vacuum-degassed heats. For heats 2 and 3, desulphurization was carried out during refining in a ladle under carbide slags. For heats 4 and 5, the calcium treatments involved feeding an iron-clad calcium silicide (Ca–Si) wire (Ca/Si = 30/60) into melts in the ladle just after vacuum degassing. Ingots of 2.6 Mg were hot-rolled to 150 mm diameter (hot-rolling reduction of 90%) at a temperature of 1473–1523 K.

The non-metallic inclusions were identified using electron probe microanalysis (EPMA). In the EPMA analysis operation the voltage and current used were 15 kV and 0.05 μm, respectively. The volume fraction of the inclusions was determined by point counting. To determine the volume fraction of inclusions, an optical microscope having a ruled 20 × 20 grid inserted in one eyepiece was used. For statistical analysis, 24 000 points were counted by taking 60 fields of view of sections parallel to the rolling direction. Inclusions on the micrographs were taken at random to measure their mean aspect ratio and mean diameter. Spheroidized inclusions were assumed to be complete spheres of mean diameter D given by [18]

$$D = \pi/2\left(\frac{\Sigma n_i d_i}{\Sigma n_i}\right) \quad (1)$$

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TABLE I Chemical composition and gas analysis of steels used

Designation of steel	Chemical composition and gas analysis (wt %)												
	C	Si	Mn	P	S	Cr	Mo	Ni	Ca	Al	Ti	O_2	N_2
Heat 1	0.40	0.18	0.72	0.013	0.016	0.78	0.21	1.71	–	0.028	0.013	0.0011	0.0110
Heat 2	0.40	0.20	0.74	0.015	0.002	0.76	0.20	1.71	–	0.030	0.013	0.0013	0.0104
Heat 3	0.40	0.19	0.73	0.015	0.0008	0.76	0.21	1.71	–	0.030	0.012	0.0011	0.0109
Heat 4	0.40	0.18	0.74	0.014	0.016	0.78	0.21	1.71	0.0059	0.029	0.013	0.0012	0.0109
Heat 5	0.40	0.20	0.73	0.014	0.002	0.76	0.20	1.71	0.0061	0.030	0.013	0.0012	0.0105

where d_i is the diameter of spheroidized inclusions appearing on the micrographs and n_i is the frequency with which they appear.

TABLE II Non-metallic inclusions of steel with commercial sulphur content level and desulphurized steels

Designation of steel	Inclusion type	V_f (%)[a]	MAR[a]
Heat 1	Stringy	0.16	16.2
	Cluster	0.036	–
	Particle	0	–
Heat 2	Stringy	0.012	2.5
	Cluster	0.025	–
	Particle	0	–
Heat 3	Stringy	0	1.7
	Cluster	0	–
	Particle	0	–

[a] V_f = volume fraction, MAR = mean aspect ratio.

3. Results and discussion

3.1. Effect of desulphurization on morphology of non-metallic inclusions

Table II gives the volume fraction and mean aspect ratio of the non-metallic inclusions in the steel with commercial sulphur content (heat 1) and desulphurized steels with low sulphur (heat 2) and ultra-low sulphur content (heat 3). The volume fraction of a stringy type of inclusion was reduced significantly with decreasing sulphur content through desulphurization. The mean aspect ratio of the inclusions also decreased dramatically with decreasing the sulphur content levels through desulphurization (Fig. 1a). In particular, for heat 3 with ultra-low sulphur content the volume fraction of the inclusions could not be evaluated by point counting, while small amounts of inclusion were observed by optical microscopy. EPMA analysis revealed that the stringy type of inclusion consisted predominantly of MnS in both heats 2

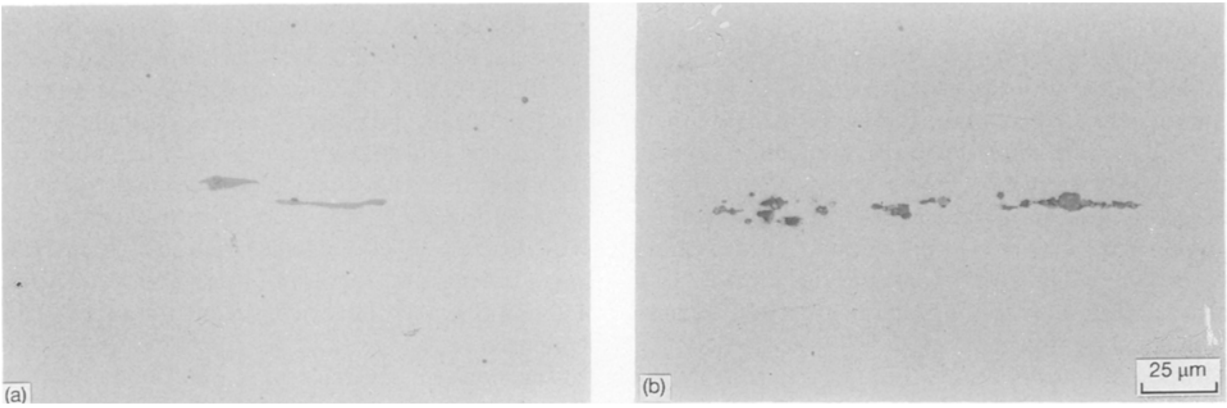

Figure 1 Optical micrographs of (a) stringy and (b) cluster types of inclusion found in heat 2.

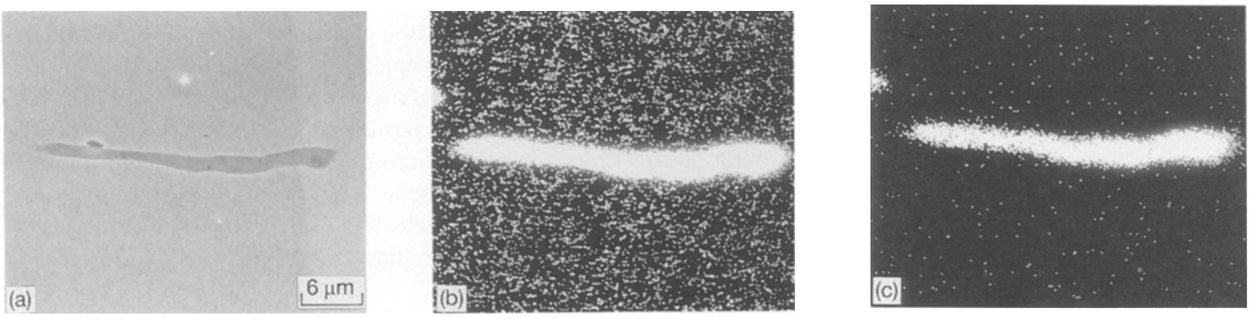

Figure 2 Example of identification of stringy type of inclusion found in heat 2 by EPMA: (a) backscattered image, (b) Mn, (c) S.

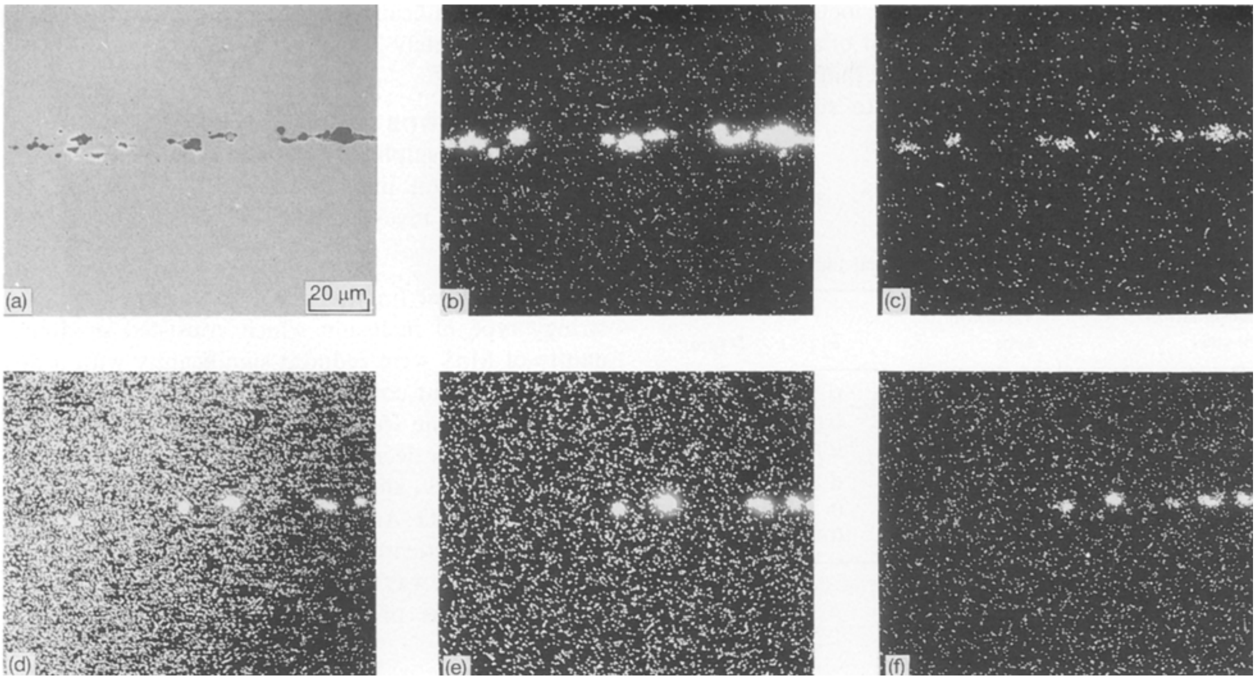

Figure 3 Example of identification of cluster type of inclusion found in heat 2 by EPMA: (a) backscattered image, (b) Al, (c) O, (d) Mn, (e) S, (f) Ca.

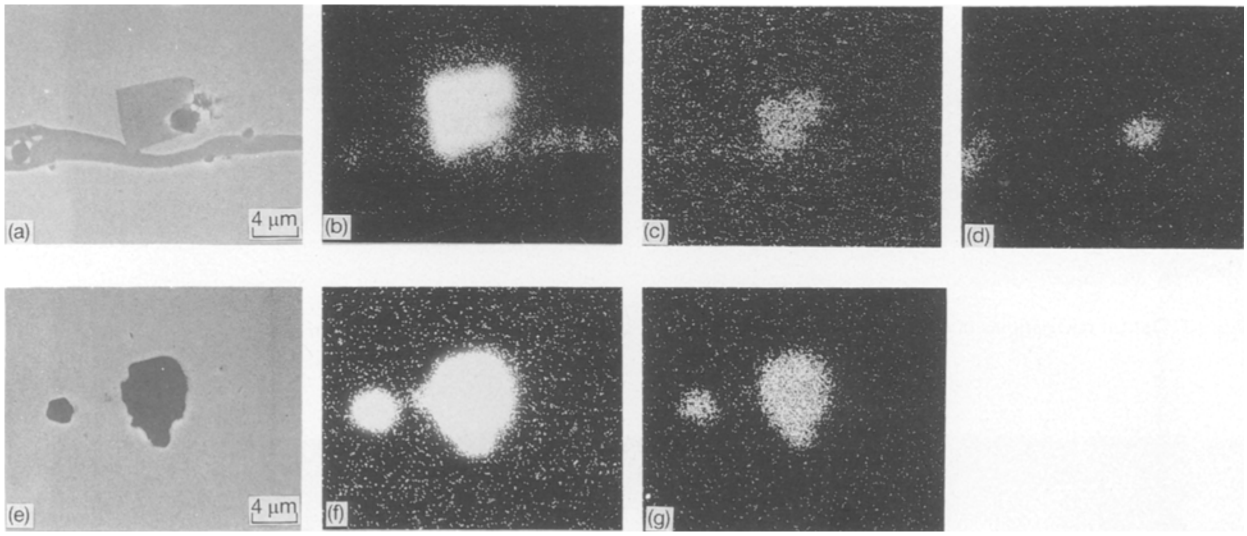

Figure 4 Examples of identification of particle type of inclusion found in heat 2 by EPMA: (a) backscattered image, (b) Ti, (c) N, (d) O; (e) backscattered image, (f) Al, (g) O.

and 3 (Fig. 2). A cluster type of composite inclusion was also reduced by desulphurization, but small amounts of the inclusion were still found in heat 2 (Fig. 1b). EPMA analysis revealed that the cluster type of composite inclusion consisted of MnS–CaS–CaO–Al_2O_3 (Fig. 3). Concerning particle-type inclusions, these could not be evaluated by point counting but small amounts were observed by optical microscopy. The inclusions consisted of TiN, TiO_2 or Al_2O_3 (Fig. 4).

3.2. Effect of calcium treatments on morphology of non-metallic inclusions

Table III gives the volume fraction and mean diameter of the inclusions in calcium-treated steels (heats 4 and 5). The calcium treatment for heat 1 with a commercial sulphur content level (heat 4) was not very effective in modifying the inclusions, producing a cluster type of inclusion (Fig. 5a). Examination by EPMA revealed two types of cluster composite inclusion: type I consisted of CaS–CaO–MnS (Fig. 6), while type II consisted of CaS–CaO–TiS–TiO (Fig. 7). However, the calcium treatment of heat 2 with low sulphur content (heat 5) significantly decreased the stringy MnS inclusions and dramatically modified the stringy type to a particle type whose mean diameter was 1.3 µm. EPMA analysis revealed that the particle type consisted predominantly of CaS–CaO, while small amounts of Ti and Al were detected (Fig. 8). Thus, it was found that modification of the inclusion morphology was controlled by the amount of added calcium. The present work has suggested that the optimum ratio of added calcium content to sulphur content (Ca/S) for modification of the inclusion morphology was approximately 3.

TABLE III Non-metallic inclusions of calcium-treated steels

Designation of steel	Inclusion type	V_f (%)	D (μm)[a]
Heat 4	Stringy	0	–
	Cluster	0.18	–
	Particle	0.010	–
Heat 5	Stringy	0	–
	Cluster	0	–
	Particle	0.054	1.3

[a] D = mean diameter.

4. Conclusions

The effect of desulphurization and calcium treatments on the inclusion morphology of 0.4C–Cr–Mo–Ni steel has been investigated. The conclusions are as follows.

1. The volume fraction and mean aspect ratio of a stringy type of inclusion which consisted predominantly of MnS were reduced significantly with a decrease in sulphur content through desulphurization.
2. The volume fraction of a cluster type of composite inclusion decreased through desulphurization, although small amounts of composite inclusion (MnS–CaS–CaO–Al_2O_3) were found.
3. Calcium treatment of a steel with commercial sulphur content was not very effective for modification of the inclusions, producing two types of the cluster

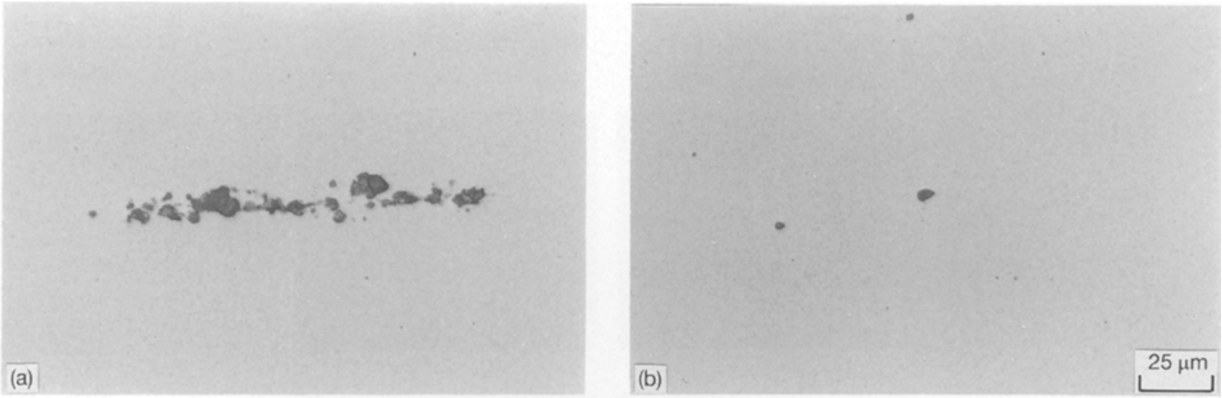

Figure 5 Optical micrographs of (a) cluster and (b) particle types of inclusions found in heats 4 and 5, respectively.

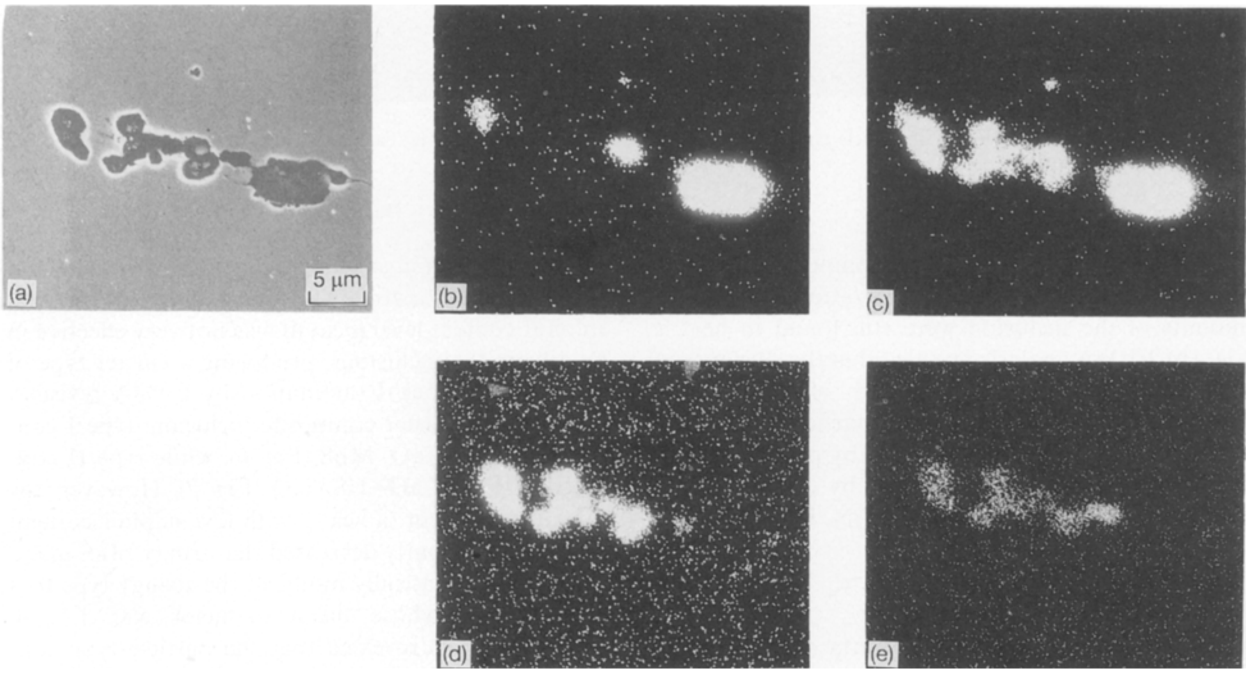

Figure 6 Example of identification of cluster type I of inclusion found in heat 4 by EPMA: (a) backscattered image, (b) Ca, (c) S, (d) Mn, (e) O.

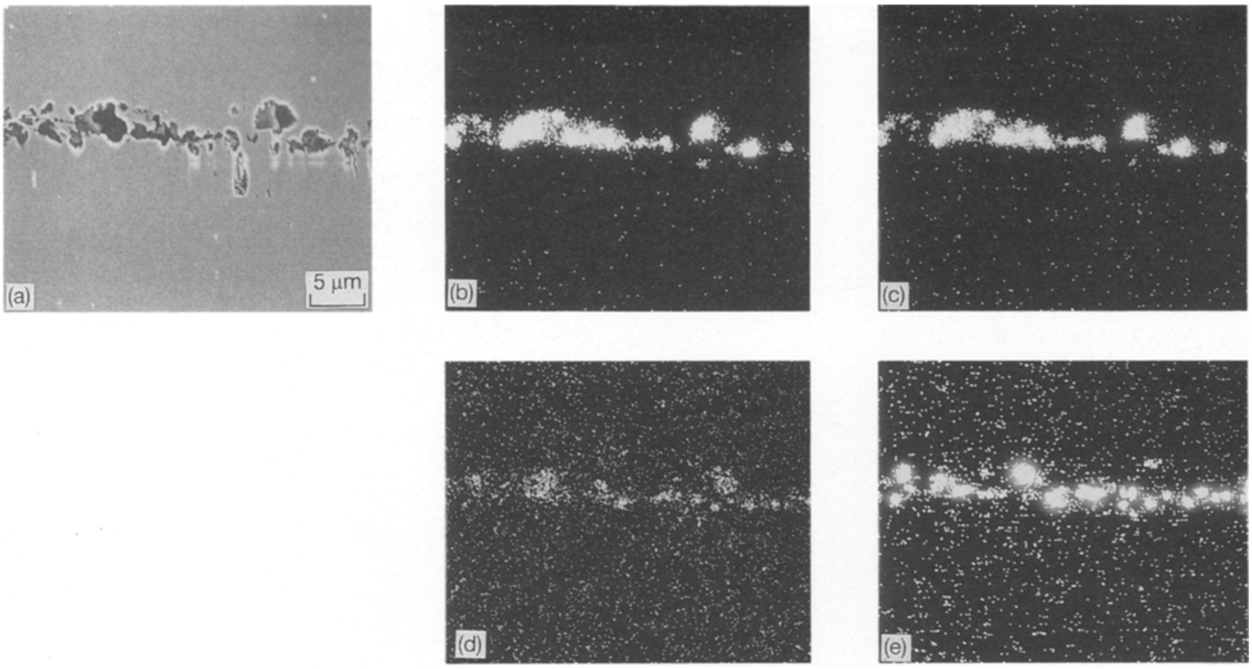

Figure 7 Example of identification of cluster type II of inclusion found in heat 4 by EPMA: (a) backscattered image, (b) Ca, (c) S, (d) O, (e) Ti.

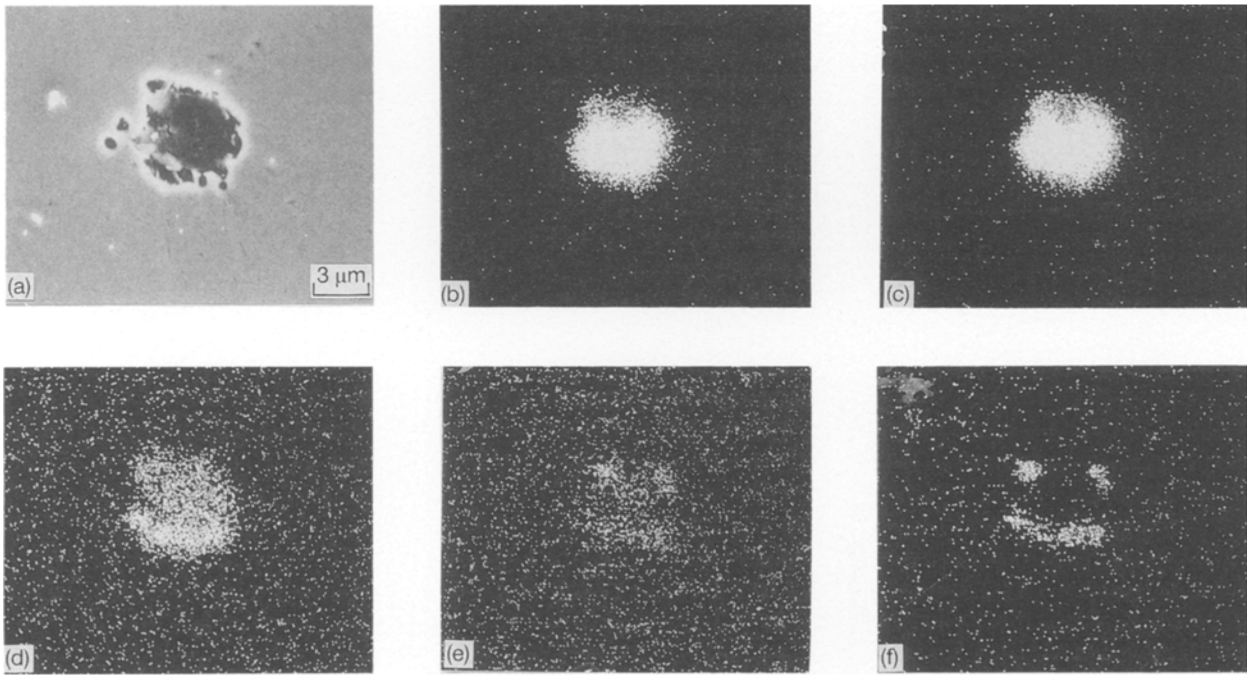

Figure 8 Example of identification of particle type of inclusion found in heat 5 by EPMA: (a) backscattered image, (b) Ca, (c) S, (d) O, (e) Al, (f) Ti.

composite inclusion: type I consisted of CaS–CaO–MnS and type II of CaS–CaO–TiS–TiO.

4. Calcium treatment of desulphurized steel modified dramatically the stringy type to a particle type (mean diameter: 1.3 µm) which consisted predominantly of CaS–CaO, while small amounts of Ti and Al were also detected.

5. The present work has suggested that the optimum ratio of added calcium content to sulphur content (Ca/S) for modification of the inclusion morphology was approximately 3.

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