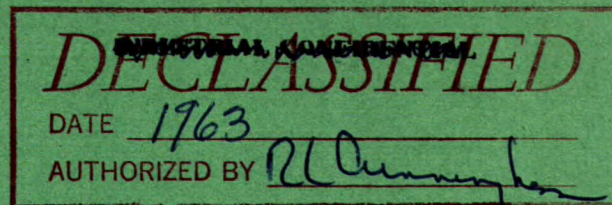


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**DEPARTMENT OF MINES AND TECHNICAL SURVEYS**

**OTTAWA**

**MINES BRANCH INVESTIGATION REPORT IR 61-109**

**INVESTIGATION OF THE OCCURRENCE OF  
INCLUSIONS IN TIN-PLATED STEEL FOR  
DOMINION FOUNDRIES AND STEEL, LIMITED,  
HAMILTON, ONTARIO**

by

**JOHN F. ROWLAND**

**MINERAL SCIENCES DIVISION**

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SUMMARY OF RESULTS

X-ray diffraction techniques, supplemented by spectrographic analysis, have been used to investigate samples of inclusions in tin-plated steel and of other materials submitted by Dominion Foundries and Steel, Limited, Hamilton, Ontario. The investigations indicated that the inclusions are composed essentially of a non-magnetic compound with the spinel structure, but its precise chemical composition could not be determined. Although the origin of the inclusions could not be determined definitely, it is most probable that they are the same kind of inclusions that were found to be present in the ingots from which the tin-plated steel was produced.

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## INTRODUCTION

In September and October, 1959, twenty-two samples were submitted to the Mines Branch by Dominion Foundries and Steel, Limited, Hamilton, Ontario (hereinafter referred to as DOFASCO). The first group of samples was delivered in person by Mr. J.I. Carrick, an employee of DOFASCO, who explained the problems which were involved. The other samples were submitted by mail, or delivered in person.

The samples submitted were of the following types: pieces of tin-plated steel containing non-metallic inclusions, fragments of refractory bricks, powdered brick samples, products obtained from dissolving tin-plated steel, material removed from a metal ingot, and a typical slag sample. The samples are individually identified in the section of this report where the X-ray diffraction interpretations appear.

The purpose of this investigation was to identify the non-metallic inclusions present in the tin-plated steel, and to compare them with possible source materials, to deduce the origin of the contamination.

Metallographic examinations were being conducted in the Ferrous Metals Section of the Physical Metallurgy Division, Mines Branch, and it was felt that further investigation using an additional technique was necessary to supplement this work.

Accordingly, the Mineral Sciences Division was approached, and it was decided to examine the samples by X-ray diffraction analysis in the Physical Chemistry Section. Spectrographic analyses were provided for some of the samples by the Metal Physics Section of the Physical Metallurgy Division, Mines Branch.

The results of the investigations were reported informally to DOFASCO as soon as they were available and, since there was the possibility of additional samples being submitted, the issuing of a formal report was postponed. In February, 1960, the author was informed by DOFASCO that the problem could be considered completed, and that the work done was appreciated. The writing of this report, which consolidates the results previously reported, was unfortunately delayed due to the urgency of other investigations being done in this Section.

## EXPERIMENTAL

### A. Techniques

#### 1. X-ray Diffraction

Specimens suitable for X-ray diffraction analysis were prepared from the samples in the following ways:-

- 1) the non-metallic inclusions were removed from the tin-plated steel with a needle, and were mounted on fine glass fibres;

- 2) portions of the refractory samples, and of the slag sample, were ground to about 300 mesh, mixed with collodion, and rolled into spindles of about 0.2 mm diameter;
- 3) the materials obtained by dissolving tin-plated steel, and the material from the metal ingot, were crushed, examined under a binocular microscope, and separated into components when not homogeneous; fragments of the various components were then mounted on fine glass fibres.

Powder diffraction patterns were obtained from the specimens using 57.3 mm diameter Debye-Scherrer cameras and filtered CuK radiation. The film for one of the specimens was too dark to be readily interpreted, due to secondary radiation generated by the fluorescence of the sample, and additional films were made using filtered Fe and filtered Cr radiations to try to eliminate this effect. The diffraction patterns were interpreted by comparison with data published in the X-Ray Powder Data File issued by the American Society for Testing Materials, or with standard patterns of relevant compounds available in the Physical Chemistry Section.

In interpreting X-ray diffraction patterns, the following limitations of the technique must be borne in mind. Crystalline constituents which are present in quantity less than about 5% of the total will probably not be detected, and those less than about 2% will almost certainly not be detected. Any amorphous material present cannot be identified, and even its presence can be detected only when a substantial amount occurs. In this investigation, the relative abundance of the constituents present was assessed merely on the

basis of the relative strengths of their diffraction patterns and, hence, this information should be considered as an approximation only. The strength of the diffraction pattern is, in fact, dependent not only on the abundance of the material giving rise to it, but also on the crystalline symmetry of the materials, their degree of crystallinity, and the chemical nature of the atoms present.

## 2. Spectrographic Analysis

Four of the samples (18-21 inclusive) were submitted to the Metal Physics Section of the Physical Metallurgy Division for qualitative spectrographic analyses. The results of this investigation, which was done by Dr. Eric Smith, are reported in Table 3, along with the X-ray diffraction results for these samples.

### B. Results

The X-ray diffraction and spectrographic analysis results are given below in Tables 1, 2, and 3; along with brief descriptions of the samples. The samples are numbered consecutively according to the dates of submission, but are grouped according to types of material in the tabulations. For the convenience of DOFASCO in comparing this report with the series of preliminary reports already issued to them, the dates of submission, Physical Chemistry Section X-ray Laboratory problem numbers, and X-ray diffraction film numbers are included.

TABLE 1

Results of X-ray Diffraction Examinations  
Non-Metallic Inclusions in Tin-Plated Steel

Date Submitted, Problem Number, Type of Samples	Sample Number, DOFASCO Markings on Samples	X-Ray Film Number	Constituents Identified by X-ray Diffraction
Sept. 8, XL-1351: Two metal discs and one polished section; source not identified.	1) Disc #1.	X8570	Major: Spinel (composition cannot be defined; see later for comments on unit-cell dimension). Minor: Tin ( $\beta$ -Sn). Possible trace: Iron ( $\alpha$ -Fe), Corundum ( $Al_2O_3$ , aluminum oxide).
	2) Disc #2.	X8571, X8573	Major: Iron. Minor: Tin, Spinel. Possible trace: Corundum.
	3) Polished section.	X8572	Amorphous or poorly crystalline material (cannot be identified).
Sept. 8, XL-1352: Four pieces of tin- plated steel.	4) Gritty, tan, 37110.	X8574	Major: Spinel. Minor: Iron, Tin. Possible trace: Corundum.
	5) Top pour, 37309.	X8575	Major: Spinel (unit-cell dimension, $a = 8.205 \text{ \AA}$ , determined accurately; same value applies to all spinel occurrences). Minor: Iron. Trace: Tin.
	6) Gritty, tan, 37460.	X8577	Major: Spinel. Trace: Iron, Tin.
	7) Gritty, light tan, 37462.	X8576	Major: Spinel, Iron. Trace: Tin, Corundum (only definite identification of aluminum oxide in the inclusions).
Sept. 12, XL-1358: Two pieces of tin- plated steel.	16) # 37685, red, smaller.	X8592, X8594	Spinel (no other constituent detected; non-magnetic).
	17) # 37685, black, larger.	X8593, X8595	Major: Spinel. Trace: Tin.



TABLE 2

Results of X-ray Diffraction Examinations  
Samples of Refractory Material

Date Submitted, Problem Number, Type of Samples	Sample Number, DOFASCO Markings on Samples	X-Ray Film Number	Constituents Identified by X-ray Diffraction
Sept. 9, XL-1353; Samples from two ladles; identified by number and supplier.	8) Ladle # 5; Stopper sleeve S148B; Haws Refractory.	X8578	Major: Mullite ( $3Al_2O_3 \cdot 2SiO_2$ aluminum silicate). Minor: Quartz ( $SiO_2$ , silica). (Plus some Amorphous material).
	9) Ladle # 9; Ladle block; Porter.	X8579	Major: Mullite. Trace: Quartz. (Plus some Amorphous material).
Sept. 9, XL-1354; Three brick samples; identified by position and supplier.	10) Ingot floor # 10; Fountain brick; Swank.	X8580	Major: Mullite. Minor: Quartz. (Plus some Amorphous material).
	11) Ingot floor # 11; Fountain brick; Porter.	X8581	Major: Mullite. Minor: Quartz. (Plus some Amorphous material).
	12) Furnace # 16; Dolomite linings; Steetley's.	X8582	Major: Lime (CaO, calcium oxide), Periclase (MgO, magnesium oxide). Minor: Portlandite ( $Ca(OH)_2$ , calcium hydroxide).
Sept. 10, XL-1356: Three samples of powdered brick; identified by use and source of material.	13) Ladle # 3; Dando bottom brick; Porter.	X8583	Major: Mullite. Large minor: Quartz. (Plus some Amorphous material).
	14) Furnace # 19; Gondol; Basic Refractories.	X8584	Major: Lime, Periclase. Minor: Portlandite.
	15) Fairset # 23; Ladles and ingot floor; A.P. Green.	X8585	Major: Mullite, Quartz. (Plus some Amorphous material).

TABLE 3

Results of X-ray Diffraction Examinations and Spectrographic Analyses  
Miscellaneous Samples

Date Submitted, Problem Number	Sample Number, Description of Material Examined	X-ray Film Number	Constituents Identified by X-ray Diffraction	Elements Detected by Spectrographic Analysis
Sept. 29, XL-1361.	18) Insoluble residue obtained from dissolving tin-plate from around a defect (representative).	X8609	Major: Cassiterite ( $\text{SnO}_2$ , tin oxide). Minor: Hematite ( $\text{Fe}_2\text{O}_3$ , iron oxide). Trace: Unidentified. Possible trace: Spinel, Corundum.	Major: Fe, Sn. Strong trace: Si, Mg, Ca, Mn, Al, Zn. Weak trace: Cr, Ni, Cu, Mo, V.
	19) Blank run from same heat; areas of tin-plate without defects (representative).	X8610	Major: Cassiterite. Minor: Hematite. Trace: Unidentified (as above). Possible trace: Spinel, Corundum.	Major: Fe, Sn. Strong trace: Si, Mg, Ca, Mn, Al, Zn. Weak trace: Cr, Ni, Cu, Mo, V.
	20) Material suspected of causing defect in the tin-plate; taken from an ingot (representative).	X8611, X8613, X8614, X8615	Major: Amorphous material (cannot be identified). Minor: Spinel; possible Manganese oxide ( $\text{MnO}$ ) but with a unit-cell dimension smaller than that of pure $\text{MnO}$ (manganosite) possibly due to solid solution of $\text{FeO}$ , $\text{MgO}$ , etc. Trace: Unidentified.	Major: Fe Si. Minor: Mg Strong trace: Ca, Mn, Al. Weak trace: Sn, Zn, Cr, Ni, Cu, Mo, V.
	21) Typical sample of slag (representative).	X8612	Major: Tricalcium silicate ( $3\text{CaO}\cdot\text{SiO}_2$ ). Minor: Manganese oxide (as above). Trace: Hematite. Possible trace: Dicalcium ferrite ( $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ ).	Major: Fe, Mg. Minor: Si, Ca. Strong trace: Mn, Al. Trace: Sn, Zn. Weak trace: Cr, Ni, Cu, Mo, V.
Oct. 13, XL-1363.	22) Insoluble residue obtained by dissolving tin-plate (representative).	X8618	Major: Brass (or bronze), with unit-cell dimension close to that of 70% Cu-30% Zn. Minor: Spinel. Trace: Graphite (carbon) (Plus large amount of Amorphous material).	
	22a) Metal fragments only.	X8620	Major: Brass. Trace: Spinel, Iron.	
	22b) White material only.	X8621	Major: Spinel. Trace: Brass.	
	22c) Black material only.	X8622	Major: Graphite. Trace: Spinel, Unidentified.	

## DISCUSSION OF RESULTS

Nine of the samples submitted (1-7 inclusive, 16 and 17) consisted of tin-plated steel containing non-metallic inclusions. The inclusion in sample 3 gave an amorphous X-ray diffraction pattern, and it could, therefore, not be identified. The X-ray diffraction films for the eight other samples, however, indicated that the inclusions are all predominantly the same spinel-type compound. The tin and iron identified in the films represent contamination of the specimen, caused by the removal of some of the tin-plated steel along with the inclusion. A trace amount of aluminum oxide (corundum) was identified in sample 7, and small trace amounts may be present in samples 1, 2 and 4. The presence of this compound may not be significant, and the inclusions are considered to be essentially the spinel-type compound.

The unit-cell dimension of this spinel was determined accurately as  $a = 8.205 \text{ \AA}$  from the diffractions present in the film obtained from sample 5, and all the other spinel occurrences appeared to have the same unit-cell dimension. The inclusion removed from sample 16, which was shown by X-ray diffraction to consist entirely of spinel, with no contamination by the tin-plated steel, was non-magnetic. It is not possible, however, to state the precise chemical composition of this compound since the spinel structure occurs in a complex solid-solution system containing

numerous combinations of atoms with almost unlimited substitution. A list of spinel-type compounds, with unit-cell dimension close to that of the spinel in the inclusions, is given below. It is likely that the spinel present in the inclusions is a solid-solution mixture of several of the compounds in the list, and since the inclusion is non-magnetic, it can be assumed that the contribution to the solid-solution mixture of the ferrites, including magnetite ( $\text{Fe}_3\text{O}_4$ ), is low.

$\text{FeO} \cdot \text{Al}_2\text{O}_3$	$a = 8.100 \text{ \AA}$	$\text{MgO} \cdot \text{Fe}_2\text{O}_3$	$a = 8.377 \text{ \AA}$
$\text{MgO} \cdot \text{Al}_2\text{O}_3$	$a = 8.106 \text{ \AA}$	$\text{ZnO} \cdot \text{Fe}_2\text{O}_3$	$a = 8.419 \text{ \AA}$
$\text{ZnO} \cdot \text{Al}_2\text{O}_3$	$a = 8.112 \text{ \AA}$	$\text{Fe}_3\text{O}_4$	$a = 8.434 \text{ \AA}$
$\text{MnO} \cdot \text{Al}_2\text{O}_3$	$a = 8.280 \text{ \AA}$	$\text{MnO} \cdot \text{Fe}_2\text{O}_3$	$a = 8.589 \text{ \AA}$
$\gamma\text{-Fe}_2\text{O}_3$	$a = 8.339 \text{ \AA}$		

Eight of the samples submitted were of refractory materials, either as large pieces of brick (8-12 inclusive), or as powdered brick (13-15 inclusive). The bricks were of the same types that had been used in the production of the tin-plated steel in the following ways:- as ladle linings (8, 9, 13 and 15), as the ingot floor (10, 11 and 15), and as furnace linings (12 and 14). The samples of the ladle and ingot floor bricks were identified as essentially the same, the X-ray diffraction patterns having been interpreted as representing large amounts of aluminum silicate (mullite) with lesser amounts of silica (quartz) and some amorphous material. The furnace lining samples were both identified as consisting of large amounts of calcium oxide (lime) and magnesium oxide (periclase)

with lesser amounts of calcium hydroxide (portlandite).

Three of the samples (18, 19 and 22) were the insoluble residues obtained after dissolving tin-plated steel in acid. Sample 22, which consisted principally of brass and amorphous material, with lesser amounts of spinel, graphite, and iron, was later found by DOFASCO to have been contaminated, and its X-ray diffraction identification is, therefore, not significant. Samples 18 and 19, respectively, were the insoluble residues obtained after dissolving tin-plated steel with and without inclusions or defects. The X-ray diffraction interpretation was the same for each, however, and the following constituents were identified: major tin oxide (cassiterite), minor iron oxide (hematite), trace unidentified, possible trace aluminum oxide (corundum) and spinel-type compound. The spectrographic analyses were also the same for samples 18 and 19, and the major elements detected, Fe and Sn, can be correlated with the iron and tin oxides, while the strong trace elements, Si, Mg, Ca, Mn, Al, and Zn, are not inconsistent with the crystalline constituents identified.

The other two samples submitted (20 and 21) were, respectively, material which had been taken from an ingot and was suspected of causing defects in the tin-plated steel, and a typical sample of slag. The X-ray diffraction investigation of the material from the ingot was complicated by the presence of large amounts of amorphous material in the sample. The crystalline constituents

were eventually identified, but not with complete certainty, as the spinel-type compound, manganese oxide (MnO) with a unit-cell dimension smaller than that of pure MnO (manganosite), and trace unidentified. The presence of compounds such as FeO or MgO in solid solution in the manganese oxide would explain the smaller unit-cell dimension. The elements detected by the spectrographic analysis cannot be readily correlated with the X-ray diffraction interpretation since the major portion of the sample consists of amorphous material, but the Fe, Mg, Mn, and Al are consistent with the crystalline constituents. The amorphous material is almost certainly a glass, and it may consist of calcium and/or aluminum silicates. The X-ray diffraction examination of the slag sample identified its constituents as a large amount of tricalcium silicate ( $3\text{CaO}\cdot\text{SiO}_2$ ), a lesser amount of manganese oxide (as above), a trace amount of iron oxide (hematite), and a possible trace of dicalcium ferrite ( $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ ). A comparison of the spectrographic analysis results and the X-ray diffraction interpretation permits the correlation of the elements Si, Ca, Mn, Al, and some of the Fe with the identified constituents, but also suggests that the compound identified as manganese oxide may actually contain large amounts of magnesium and iron.

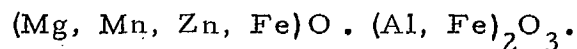
It would appear that the weak trace elements Cr, Ni, Cu, Mo, and V, which were detected in all the spectrographic analyses, have no significance, other than their occurrence as trace constituents

of the steel.

It is most probable that the inclusions in the tin-plated steel are the same kind of inclusions that are present in the metal ingots, since sample 20, which was material which had been taken from an ingot and was suspected of causing defects in the steel, contained the only other occurrence of spinel. It is considered unlikely that the furnace linings, the only refractory bricks which contained an element (magnesium) suitable for spinel production, reacted with the molten metal to form this compound, which was then introduced into the steel as inclusions, since the spinel is apparently low in ferrite content.

#### CONCLUSIONS

The investigations indicated that the inclusions in the tin-plated steel are composed essentially of a compound with the spinel structure, which is non-magnetic. The precise composition of this compound is indeterminate, although the unit-cell dimension,  $a = 8.205 \text{ \AA}$ , combined with the composition of other compounds identified in the samples, suggests a possible formula of



The proportions of the metal atoms are unknown, but the amount of iron present is low since the compound is non-magnetic. A

small amount of aluminum oxide (corundum) may be present along with the spinel. The origin of the inclusions cannot be determined definitely.

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