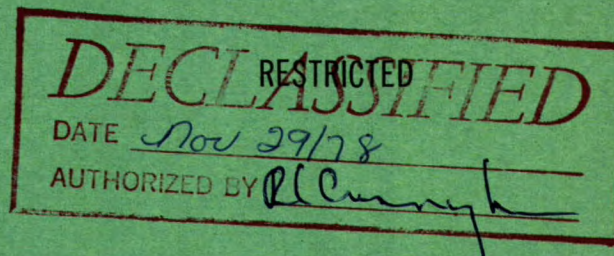


This document was produced
by scanning the original publication.

Ce document est le produit d'une
numérisation par balayage
de la publication originale.



CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 59-15

X-RAY DIFFRACTION INVESTIGATIONS ON A PIECE OF
TURBINE BLADE SUBMITTED BY THE BRITISH COLUMBIA
RESEARCH COUNCIL

by

J. F. ROWLAND

MINERAL DRESSING AND PROCESS METALLURGY DIVISION

Mines Branch Investigation Report IR 59-15
X-RAY DIFFRACTION INVESTIGATIONS ON A PIECE
OF TURBINE BLADE SUBMITTED BY THE BRITISH COLUMBIA
RESEARCH COUNCIL

by

J. F. Rowland^{*}

- - - -

SUMMARY OF RESULTS

An X-ray diffraction investigation has been made in an attempt to identify the coatings present on a piece of a turbine blade. A flakey black scale was shown to be nickel oxide, and a thin green film occurring beneath the scale contained phases having a spinel and a "dititanate" structure, along with, possibly, some nickel oxide.

The alteration of the underlying metal, and the formation of the coatings, appeared to be due to preferential oxidation.

^{*}Scientific Officer, Mineral Dressing and Process Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

CONTENTS

	<u>Page</u>
Summary of Results	i
Introduction	1
Experimental Techniques	2
Experimental Results	3
Discussion of Results	4
Conclusions	8
Figure 1	9
Appendix	10

= =

13 pages, 1 Figure, 1 Appendix

INTRODUCTION

During October 1958, a piece of a turbine blade was submitted to the Mineral Dressing and Process Metallurgy Division, Mines Branch, by Dr. A. W. Greenius of the Division of Engineering, British Columbia Research Council. The turbine blade, which had been removed from a Britannia aero-engine, had been supplied originally by Bristol Aero Engines (Western) Limited. A black scale had been noticed on blades taken from engines during a first overhaul, and this deposit had been removed by vapour-blasting before the blades were re-installed. During a second overhaul a thin green film was noticed beneath this flaking black scale, and overlying apparently altered base metal. The blade alloy was stated to be Nimonic 100, which has a nominal composition of C, 0.3% max.; Ti, 1.0-2.0%; Cr, 10-12%; Al, 4-6%; Si, 0.5% max.; Fe, 2.0% max.; Co, 18-22%; Mo, 4.5-5.5%; and Ni, balance.

A part of a turbine blade, with the coatings present on the concave surface, was referred to the Physical and Crystal Chemistry Section of the Mines Branch for an X-ray diffraction investigation. No work was done on a whole blade, also submitted, from which the coatings had been removed.

Previous work done by the British Columbia Research Council, included a general metallographic examination, and X-ray fluorescence and X-ray diffraction analyses. A photomicrograph, Figure 1 (see page 9), showing the metallographic structure of the black scale, the green film, the underlying altered metal, and the base metal, accompanied the turbine blades. An explanatory letter from Dr. Greenius to the Mines Branch is given as an Appendix. The

X-ray fluorescence analysis showed that there had been, apparently, no contamination of the blade surface. The X-ray diffraction analysis had been done by direct reflection of the X-ray beam from the curved surface of the blade. The consequent displacement of the diffractions made their interpretation impossible, and hence the coatings could not be identified.

EXPERIMENTAL TECHNIQUES

The X-ray diffraction analysis was done in the Physical and Crystal Chemistry Section using 57.3 mm. diameter Debye-Scherrer powder cameras with filtered FeK radiation. The specimens examined were obtained by removing small amounts of the coatings, and of the base metal, from the turbine blade, and then mounting each of these materials on the end of a glass fibre. The glass fibres were inserted into brass spindles which were placed co-axially in the powder cameras. The diffraction patterns obtained were interpreted by direct comparison with available standard films, or by comparing the measured spacings with those given in the A.S.T.M. Card Index of X-ray Diffraction Patterns. Calculations made from the measured spacings gave the cell dimensions of the cubic patterns which were present, and these are quoted where the identification of the material giving rise to the pattern is not precise.

In interpreting X-ray diffraction patterns, certain points must always be borne in mind. Any amorphous material present cannot be identified, and even its presence can only be detected when a substantial amount occurs. The relative abundance of the crystalline materials present is assessed merely on the basis of the relative strengths of their X-ray diffraction patterns, and must be

considered only as an approximation. Crystalline materials present in amounts less than 5-10% of the total will probably not be detected and, if present in amounts less than 2-5%, will almost certainly not be detected. Several of the phases observed in this investigation could not be specified precisely as to composition, owing to the fact that they are members of solid solution systems. The calculated cell dimensions, combined with a knowledge of the elements present, indicated, however, probable compositions for these phases.

EXPERIMENTAL RESULTS

The X-ray diffraction pattern of the base metal, which was obtained from metal particles taken from a deposit-free part of the turbine blade, consisted of two cubic patterns, as follows:

Major: body-centred with cell dimension, $a = 2.88 \text{ \AA}$,

Minor: face-centred with cell dimension, $a = 3.57 \text{ \AA}$.

X-ray diffraction patterns were obtained from two specimens of the thin green film. The first specimen, which included particles of the underlying metal, contained the following phases:

Major: 1) nickel oxide (NiO),
2) body-centred cubic with $a = 2.88 \text{ \AA}$,
3) spinel with cell dimension close to that of magnetite,

Minor: 1) face-centred cubic with $a = 3.52 \text{ \AA}$,
2) "dititanate"* close to pseudobrookite,

Trace: unidentified material.

The second specimen of the green film, which was considered to be relatively free from contamination by particles of the underlying metal, contained the following phases:

*The term "dititanate" is defined on page 6 .

Major: 1) nickel oxide (NiO),
2) spinel with cell dimension close to that of magnetite,

Minor: 1) body-centred cubic with $a = 2.88 \text{ \AA}$,
2) "dititanate" close to pseudobrookite,

Trace: unidentified material.

A representative specimen of the flakey black scale with, however, some of the green material adhering to its interior surface, contained the following phases:

Major: nickel oxide (NiO),

Minor: spinel with cell dimension close to that of magnetite,

Trace: unidentified material.

A second specimen of the black scale, which was prepared from material in the outer surface only, to avoid any contamination, contained the following phases:

Major: 1) face-centred cubic with $a = 3.57 \text{ \AA}$,
2) body-centred cubic with $a = 2.88 \text{ \AA}$,

Minor: nickel oxide (NiO),

Trace: unidentified material.

DISCUSSION OF RESULTS

The unaltered metal consists of a body-centred cubic phase with cell dimension, $a = 2.88 \text{ \AA}$, and a face-centred cubic phase with cell dimension, $a = 3.57 \text{ \AA}$. Although the body-centred cubic phase has a cell dimension close to that of α -iron, $a = 2.867 \text{ \AA}$, this agreement is considered to be coincidental. This phase is most probably a nickel-chromium alloy; such an alloy with this structure and cell dimension has been described, although the exact composition was not specified. The cell dimension of the face-centred cubic

phase is not very different from that of pure nickel, $a = 3.524 \text{ \AA}$; however, the difference is considered to be significant. This phase, therefore, is probably a nickel alloy, with unspecified minor constituents. An iron-nickel alloy with this structure and cell dimension has been reported, but the amount of iron in Nimonic 100 is too small to justify such an interpretation. Both cubic phases, therefore, are considered to be nickel alloys, although the exact compositions cannot be stated.

Since it was not possible to obtain a specimen of the underlying alloy, in which alteration had been observed to occur, without contamination by unaltered metal, some indication of the nature of the alteration products was obtained from the diffraction pattern of the impure specimen of the green film. The altered metal appears to consist of a body-centred cubic phase, with the same cell dimension as that for the unaltered metal, and a face-centred cubic phase with a cell dimension, $a = 3.52 \text{ \AA}$, which is different from that for the unaltered metal, and close to that of pure nickel. The alteration process appears, therefore, to affect only the face-centred cubic constituent of the base metal, and apparently consists of preferential removal of the elements other than nickel, probably by oxidation.

The thin green film apparently consists of the following compounds:

- 1) nickel oxide (NiO),
- 2) a spinel phase,
- 3) a "dititanate" phase,
- 4) a body-centred cubic phase.

Since nickel oxide is later shown to be the chief constituent of the

black scale, it is possible that its occurrence in the green film is due to contamination. Since the impurities present, however, were more probably metal particles, it is likely that nickel oxide is truly present to some extent in the green layer. Although nickel oxide is generally black in colour, it has also been reported to occur with a green colour. It is probable, however, that the green colour of this thin film is caused, to a greater extent, by the presence of the spinel phase. It may be noted that nickel chromite, a spinel, is dark green in colour.

The cell dimension of the spinel phase, which probably forms the major portion of the green film, was not determined precisely, but it is not far removed from that of magnetite, Fe_3O_4 , which has a cell dimension, $a = 8.434 \text{ \AA}$. There is a wide range of possibilities for the composition of this phase, but it is probably reasonable to consider it as $(\text{Ni}^{II}, \text{Co}^{II}, \text{Fe}^{II})\text{O} \cdot (\text{Fe}^{III}, \text{Cr}^{III})_2\text{O}_3$. The oxidation conditions, which are considered to have been present during the formation of these coatings, suggest that there is little divalent iron present in the spinel, and, therefore, this phase is probably a nickel-cobalt ferrite-chromite.

An important, though not major, portion of the green film was identified as "dititanate". This term is used to designate a member of a solid solution series of complex titanium compounds, $(\text{Fe}^{II}, \text{Ca}^{II}, \text{Mg}^{II})\text{O} \cdot 2\text{TiO}_2 - (\text{Fe}^{III}, \text{Al}^{III}, \text{Ti}^{III})_2\text{O}_3 \cdot \text{TiO}_2$. The X-ray diffraction patterns indicate that the member of this series which occurs in the green film is close to pseudobrookite, Fe_2TiO_5 , in composition. The occurrence of this compound is compatible with the assumed oxidizing conditions, and with the titanium present in

Nimonic 100. It is likely that the turbine blade had been exposed to a moderately high temperature in order that the oxidation product of the iron, Fe_2O_3 , should have combined with the oxidation product of the titanium, TiO_2 .

The body-centred cubic phase, which was observed in both specimens of the green film, may represent contamination, or may be present there as an actual constituent of the film, while the face-centred cubic phase, which was observed only in the specimen known to be impure, is almost certainly due to contamination by the underlying alloy. The trace of unidentified material showed the same X-ray diffraction pattern in both specimens of the green coating.

The flakey black scale is, apparently, essentially nickel oxide (NiO). The spinel phase identified in the first specimen of the black scale is the same as that occurring in the green film, and is due to some of this green material adhering to the bottom surface of the flake. The presence of the cubic phases in the specimen taken from the outer surface of the black scale is not readily explained, however. The cell dimensions correspond with those of the constituents of the base metal, and it is possible that contamination may have occurred during specimen preparation, even though great care was taken to prevent it. It is also possible, however, that these phases represent particles of the original turbine blade, actually present in the black scale, which were not affected by the processes which formed the black and green coatings.

In all the X-ray diffraction patterns, the traces of unidentified materials were represented by a few weak diffractions only, and, except where otherwise stated, were different in each case.

CONCLUSIONS

Both the flakey black scale and the thin green film are the result of oxidation, and both nickel oxide and a spinel phase are logical oxidation products. The occurrence of a "dititanate" phase is not so readily expected as a corrosion product, but its occurrence is reasonable. The alteration of the underlying metal appears to be due to preferential oxidation, although no attempt has been made to suggest which constituents of Nimonic 100 are more readily attacked.

- - - -

(Figure 1 follows on page 9)
(Appendix follows on pages 10-11)

JFR/DV

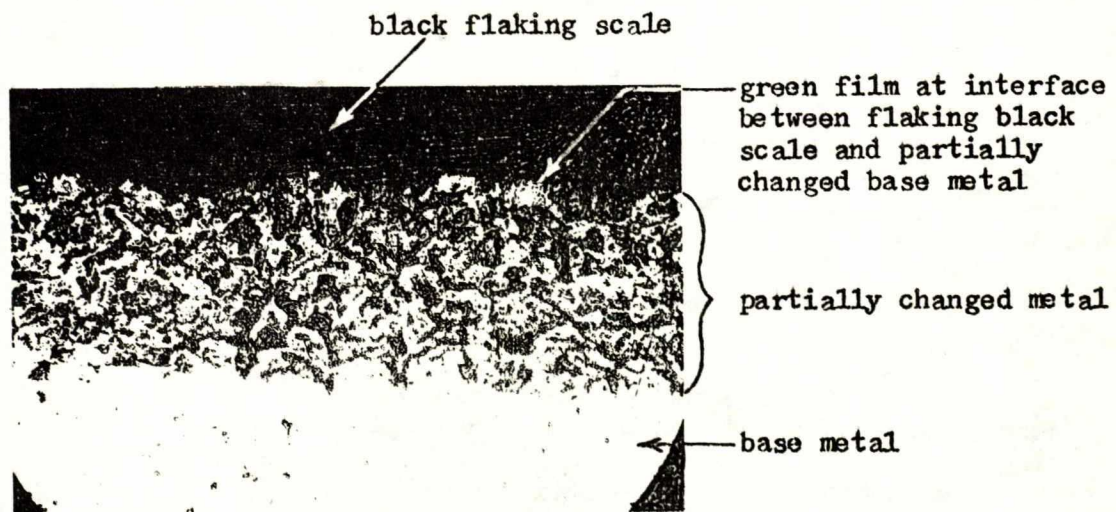


Figure 1 - Polished cross-section of Nimonic 100 turbine blade showing scaling on concave surface of blade.

(Magnification not specified)

APPENDIX

BRITISH COLUMBIA RESEARCH COUNCIL
UNIVERSITY OF BRITISH COLUMBIA
VANCOUVER 8, B. C.

October 6, 1958.

Dr. A. T. Prince,
Chief, Mineral Dressing and Process
Metallurgy Division,
Department of Mines and Technical Surveys,
552 Booth Street,
Ottawa, Ontario.

Dear Sir:

We have been asked by a Sponsor, Bristol Aero Engines (Western) Limited, to determine the nature of the black and green coatings on turbine blades removed from a Britannia aero-engine. However, we have been unable to satisfactorily identify the coatings with the techniques available to us here. Mr. Don Faurschou from the Physical Metallurgy Division who, as you may know, is on loan to us has suggested that your Division may be able to assist us.

The sponsor fears that his previous overhaul and inspection techniques (vapour-blasting, cleaning in Varsol (Imperial Oil solvent), immersion in Zy-glo penetrant, possibly inadvertently coating with Rust-Ban (Imperial Oil rust preventative) and subsequent test running) may have resulted in contamination and attack on the blades. The Sponsor reports that only the black coating was noticed on blades taken from the engines in for first overhaul, whereas the green film beneath the flaking black scale was noticed on blades taken from the engines on the second overhaul. During the first overhaul, the blades had been vapour-blasted, inspected as above, and reinstalled. Since we did not see these blades before vapour-blasting, we cannot personally verify the absence of the green film.

In addition to a general metallographic examination, we have used X-ray fluorescence and X-ray diffraction directly on the blade in determining any contaminants on the blade surface and the nature of the black and green scale or film, whether oxides, sulphides, etc. No contaminants (including vanadium, which is often suspect) were shown by the fluorescence technique. The X-ray diffraction tests on the green-coloured surface were, of necessity, carried out on the curved surface of the blade with consequent displacement of the lines. We have thus not been able to identify the coatings. Our X-ray department is not equipped to carry out Debye-Scherrer photographs of powdered particles scraped from the

black and green surfaces. Mr. Faurschou mentioned that your Division, and especially Dr. N. F. Bright or Mr. John Rowland would be able to assist us. Perhaps comparative exposures of black scale, green film, attacked metal immediately below film, and the basis metal may reveal significant differences.

A photomicrograph showing the metallographic structure of black scale, subscale, and basis metal is enclosed. A whole blade (vapour-blasted) and part of a blade (as removed from engine) are being sent under separate cover. The blade alloy is Nimonic 100, with a nominal composition of carbon, 0.30 max.; titanium, 1.0 to 2.0; chromium, 10 to 12; aluminum, 4 to 6; silicon, 0.5 max.; iron 2.0 max.; cobalt, 18 to 22; molybdenum, 4.5 to 5.5; and nickel, balance.

Any assistance that you may be able to give us will be greatly appreciated. If you should feel that this job is more properly handled by the Physical Metallurgy Division will you kindly refer it to them.

Yours very truly,

BRITISH COLUMBIA RESEARCH COUNCIL

A. W. Greenius,
Division of Engineering

Encl.