Crystal-structure of a natural nickel-iron alloy.

By Professor E. A. OWEN, M.A., Sc.D., and B. D. BURNS, M.Sc.

University College of North Wales, Bangor.

[Read June 8, 1939; communicated by the editor.]

1. *Introduction.*

NATURAL nickel-iron alloys have been found in several places on the earth's surface. In addition to alloys containing a low percentage of nickel (about 3%), there are others which contain much higher percentages of nickel (about 70%). To alloys of the latter group the name awaruite is now generally given and it may include josephinite, souesite, and other alloys possessing high nickel content so long as they belong to the same phase and possess identical crystal-structures.

It is of interest to the mineralogist to know whether these alloys conform to the structure of nickel-iron alloys prepared in the laboratory and whether they fit into the accepted phase diagram of the nickel-iron system. It is of interest also to the physicist and the metallurgist to obtain information concerning these natural alloys, because some nickel-iron alloys made in the laboratory are difficult to prepare in a state of true equilibrium. Data derived from the study of the natural alloys may help to throw light upon the structure of these artificial alloys.

2. *Previous Work on Natural Nickel-iron Alloys.*

Several investigations of natural nickel-iron alloys have been described. W. H. Melville[1] records the examination of magnetic pebbles discovered in large quantities in the gravel of a stream in Josephine and Jackson Counties in Oregon. The pebbles had smooth surfaces, coloured greenish-black and interrupted by slight areas of greyish-white alloy of nickel and iron. Upon analysis this alloy was found to contain 23·22% of iron and 60·45% of nickel by weight, which, the author points out, corresponds with the formula Fe_2Ni_5. The name josephinite was given to the material.

Another investigation on pebbles of 'josephinite' from Josephine County was carried out by G. S. Jamieson,[2] who found the alloy to be of a spongy nature, binding together and enclosing particles of serpentine.

[1] W. H. Melville, Amer. Journ. Sci., 1892, ser. 3, vol. 43, p. 509.

[2] G. S. Jamieson, ibid., 1905, ser. 4, vol. 19, p. 413.

The material on analysis yielded 25·24% of iron and 74·17% of nickel, with other elements, the chief of which was cobalt.

Souesite, a mineral containing 22·02% of iron and 75·50% of nickel, found in British Columbia, was examined by G. C. Hoffmann.[1] The nickel-iron alloy in this mineral was found in the form of small very irregularly shaped, rounded grains (maximum diameter about 1·5 mm.) of a faint yellowish steel-grey colour. It was malleable and strongly magnetic.

The original 'awaruite' from New Zealand examined by W. Skey in 1885 contained 31·02% of iron, 67·63% of nickel, and 0·70% of cobalt. The ratio of the number of nickel to the number of iron atoms in each of these minerals is given in the following table.

Mineral.	Atomic ratio (Ni/Fe).
Awaruite, New Zealand (Skey)	2·07
Josephinite, Oregon (Melville)	2·48
Josephinite, Oregon (Jamieson) ...	2·80
Souesite, British Columbia (Hoffmann)	3·26

Jamieson suggested that since all the minerals seemed to exhibit a certain uniformity of composition, the name 'awaruite' should alone be used for these terrestrial nickel-iron alloys, rich in nickel, even though there was no evidence that a definite compound of nickel and iron existed.

3. Material.

The material used in the present investigation was received from Dr. Fletcher Watson of Harvard College Observatory, Cambridge, Massachusetts, through the kindness of Professor Charles Palache of the Department of Mineralogy, Harvard University. It is recorded in Harvard Museum as being awaruite from Grant's Pass, Josephine County, Oregon, U.S.A., the Harvard number being 81,539. It was stated to contain between 70 and 75% by weight of nickel.

The sample received for examination weighed about 13 grams and was of a prolate spheroidal shape, the major axis measuring about 20 mm., and the minor axis about 14 mm. Its outer surface was covered with a smooth vitreous layer and was in places dented. When scratched with a file it showed metallic lustre. The material was somewhat brittle, but on filing it yielded a fine powder which was dark in colour owing probably to the presence of impurity, which will be assumed to consist mainly of serpentine. It was difficult to prepare a surface satisfactorily polished on account of the hardness of the material. A carefully prepared surface when examined under moderately high power showed the

[1] G. C. Hoffmann Amer. Journ. Sci., 1905, ser. 4, vol. 19, p. 319.

existence of a large number of fine cracks together with a few of larger size.

4. *Occluded Gases.*

Part of the technique in preparing powder for X-ray examination is to heat the powder gently in a tube connected directly to a pump capable of maintaining a vacuum of about 0·001 mm. of mercury. During this operation it was discovered that a comparatively large quantity of gas was discharged by the material, the gas being emitted in bursts, as seen by the disturbance of the powder which at intervals was greatly agitated by the expulsion of the gas.

A careful analysis of the gas emitted was conducted by Professor W. M. Travers of Bristol University, to whom we are greatly indebted. The weight of specimen used for this purpose was 1·5 gm. It yielded 7·5 c.c. of gas which consisted of hydrogen and carbon monoxide in equal proportions, the amount of the residual gas, the nature of which is unknown, being less than 0·05 c.c. The density of the alloy, the measurement of which is referred to below, was found to be 6·6 gm. per c.c., so that the volume of 1·5 gm. is approximately 0·25 c.c. The material therefore yields at least 30 times its own volume of gas, half of which is hydrogen and half carbon monoxide. Hydrogen mainly was displaced at the start, but on prolonging the heating more carbon monoxide was evolved.

As the temperature of a specimen of the material in powder form was raised from room-temperature to about 900° C., gas was discharged at all temperatures. The average rate of discharge was slow at first, increasing to a maximum at about 400° C.

5. *Density.*

Owing to the presence of occluded gases, and the small amount of material available, difficulty was experienced in making an accurate determination of and in reaching finality concerning the density of the material. Many observations were made with material both in lump and in powder form, in the degassed and in the original condition, by weighing in water in some cases and in paraffin oil in others. The following gives a summary of the determinations made of the density.

Condition of Material.	Density gm. per c.c.
(1) Original lump, without any treatment	6·58
(2) Portion of lump, after being degassed	6·65
(3) Powder, after being degassed ...	6·70

Taking into account that the original lump under (1) was of greater mass than the degassed portion under (2), and that not a great quantity of powder was available for the determinations under (3), the value of the density was taken to be 6·6 gm. per c.c. This value is very much lower than the density (8·5 gm. per c.c.) of an artificially prepared alloy of the same nickel content.

6. *X-ray examination.*

For the X-ray examination a small quantity of filings was taken, the filings having passed through a sieve of 100 mesh. The powder specimens were mounted on a glass fibre which was rotated at the centre of a circular camera, along a diameter of which a beam of X-rays was passed. The beam fell on the powder specimen, and on the photographic film a spectrum was obtained which was characteristic of a face-centred cubic structure. The specimens examined were submitted to various treatments before irradiation. The spectra reproduced in fig. 1 were obtained with powder specimens which were in the following conditions: (1) specimen not submitted to any treatment; (2) specimen partly degassed by heating gently while in vacuo for about fifteen minutes; (3) specimen given the same treatment as (2) but afterwards annealed at 300° C. for seven days; (4) specimen thoroughly degassed and annealed at 300° C. for seven days; (5) specimen not degassed but annealed for two weeks at 300° C.; (6) specimen thoroughly degassed and annealed for two weeks at 300° C. Spectra (1) to (4) were obtained with cobalt and (5) and (6) with iron radiation. In each case the specimen was allowed to cool in the furnace after the annealing treatment. It cooled from 300° C. to room-temperature in about three hours.

These six spectra yield parameters that are identical within the accuracy of measurement, but the width of the lines progressively decreased from (1) to (4), which is to be expected, as the distortion produced by the cold-work done in preparing the filings will be gradually removed by the heat-treatment. The removal of the gas occluded in the specimen also improves the definition of the lines, as will be observed by comparing spectra (1) and (2). The material, however, is still in a distorted condition even after the heat-treatment given to it under (4) or (6). It is accentuated in (6) owing to the more open spectrum obtained with iron radiation.

The work on artificial nickel-iron alloys in the region of composition 70 atomic % nickel, has shown that spectra characteristic of a face-centred cubic structure are obtained whatever the temperature of anneal-

ing. This is the case with alloys in a pure phase. It was therefore decided, in view of the distorted condition in which the specimens were found after the heat-treatment already mentioned, to submit samples of the material to annealing treatments at higher temperatures and for
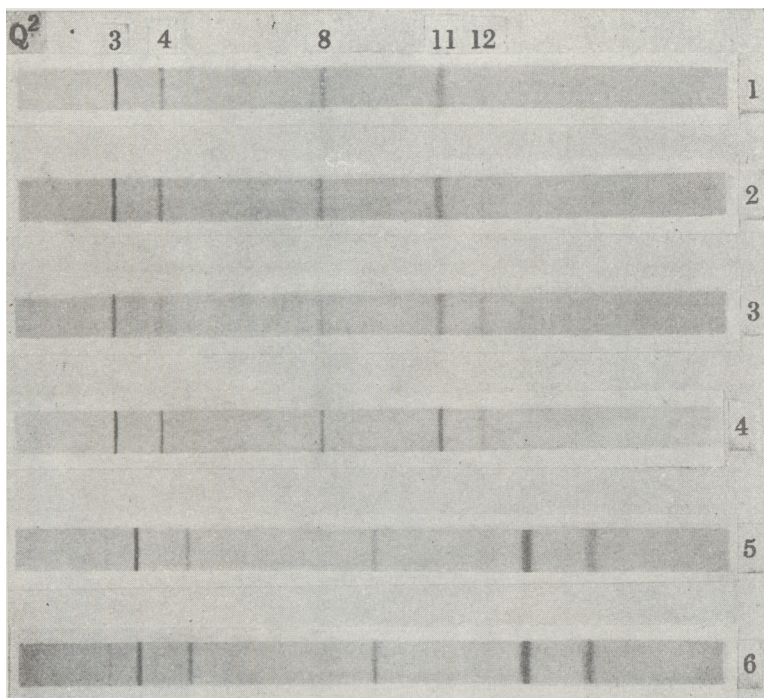

FIG. 1. X-ray powder photographs of nickel-iron alloy.

longer periods. The spectra reproduced in fig. 2 were obtained with powder specimens which had been given the following treatments: (1) annealed for eight days at 500° C. and air cooled, cobalt radiation with iron filter; (2) same treatment, but spectrum obtained with iron radiation and manganese filter; (3) same treatment as (1) and (2) followed by an additional three weeks annealing at 350° C. and air cooled, cobalt radiation with iron filter; (4) specimen of pure nickel-iron alloy containing 73% by weight of nickel, annealed for five months at 500° C., cobalt radiation with iron filter. The iron filter is not essential when irradiating a nickel-iron alloy with cobalt radiation, but with it the background is improved.

The lines in this series of spectra are well defined, showing that the material after the heat-treatment, to which it was submitted, had lost most of the distortion which existed after the first heat-treatment. Spectrum (2) was taken with iron radiation for greater accuracy in measurement and also as a check on spectrum (1) in which faint lines were to be observed. These lines were found also in the second spectrum, and will be referred to later. The longer annealing given to the specimen
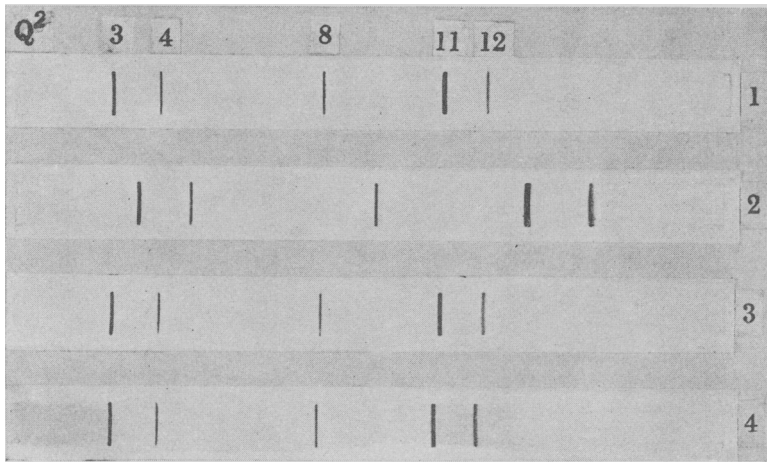

FIG. 2.   X-ray powder photographs of nickel-iron alloy.

which yielded spectrum (3) with cobalt radiation shows the reflection from the (222) plane to be almost resolved into its components a_1 and a_2. The resolution of the doublet is complete in the reflection from this plane in the spectrum of the artificial alloy. All the spectra are identical in that they indicate the presence of a face-centred cubic structure, and the parameter of the alloy in awaruite, as far as can be judged from the spectra, is the same after each heat-treatment. All the spectra containing well-defined lines contained faint lines in addition to the normal set of lines from the face-centred cubic lattice. No additional lines were observed in the spectrum of the artificial alloy (4, fig. 2).

To arrive at an accurate value of the parameter of the crystal lattice other photographs were taken with a focusing camera, with which it was possible to obtain lines at very large angles of reflection. The mean of several determinations gave 3·5516Å. for the parameter of the natural alloy at 15° C.

7. *Chemical Analysis.*

It was decided at this stage to submit the material to careful chemical analysis to ascertain the exact amount of iron present in relation to the amount of nickel, also the total amount of impurity. Analyses were carried out on two separate samples by Mr. R. Johnston of the Midland Laboratory Guild (1928) Ltd., Birmingham, who reports:

The mineral was dissolved in a mixture of three parts of hydrochloric acid and one of nitric acid, and when it was so far dissolved that all action appeared to have ceased the assay was evaporated on a water-bath to dryness, and then baked well. It was then taken up with dilute hydrochloric acid, and the insoluble residue filtered off and kept (Residue 'A').

The filtrate was treated with hydrogen sulphide and any resulting precipitate filtered off. The liquid was boiled free from the gas, oxidized, and made up to an exact bulk. Aliquot portions of this bulk were measured off for the assays of nickel and iron.

The portions for iron were precipitated with ammonia and the ferric hydroxide filtered off and dissolved in hydrochloric acid, reduced in the cold with hydrogen sulphide, boiled free, cooled and titrated with potassium dichromate using diphenyl ammine as internal indicator.

The nickel portions were evaporated to about 5 c.c. and 5 gm. of solid ammonium chloride added to each. Then the iron was precipitated with 50 per cent. ammonia and filtered off, and washed with dilute ammonia water containing ammonium chloride. The iron hydroxide was redissolved, evaporated, and treated as before, and yet again, the filtrates being added together. This triple precipitation was carried out to ensure that all the nickel was freed from the iron. The faintly ammoniacal nickel solution was warmed to about 70° C. and the nickel precipitated with alcoholic dimethylglyoxime and digested for one hour. The oxime filtered on to a Gooch crucible, washed, and dried at 120° C. and weighed when cool.

Residue 'A' was weighed, and then fused with potassium bisulphate and leached out with dilute sulphuric acid. The unaffected residue was filtered off and washed, and the iron in the filtrate determined as before by titration. The resulting iron was added to the total. The final insoluble residue was white, and we assumed that it was silica or the like, and not carrying any iron. However, fusion with soda would be needed to be absolutely sure of this, though it is hard to suppose that iron would withstand the action of fused bisulphate at a red heat.

In view of the small amount of sample available, the accuracy of the method would be $\pm 0.05\%$ for the nickel, and $\pm 0.10\%$ for the iron. Probably the results are well within these limits.

The first sample submitted for analysis was a lump of the original specimen weighing 1·8248 gm., about half the surface of which was covered with a layer of vitreous material (this being the outer surface of the original specimen) and the remainder of the surface was freshly cut. The analysis showed that the absolute percentages were as follows by weight:

Iron   ...   ... $26.90 \pm 0.10\%$ ⎫
Nickel ...   ... $57.25 \pm 0.05\%$ ⎬ atomic ratio Ni/Fe = 2·01
Impurities ...   15·85 (by difference). ⎭

After solution in acids there was filtered off a dark red powdery residue. With 1·8248 gm. of specimen this residue weighed 0·2304 gm. or 12·6% of the original weight. This was then fused with potassium bisulphate ($KHSO_4$) and leached out. The iron thus recovered amounted to 0·1178 gm. or 6·46% of the original weight of the specimen. This is included in the iron content given in the above analysis. It is possible that some of the iron found in the insoluble residue may not be alloyed.

In order to arrive at more definite results, another sample was submitted for analysis. The vitreous layer was removed and the material thoroughly degassed before commencing the analysis. This sample yielded the following absolute percentages:

Iron   ...   ... $26·50_6 \pm 0·10\%$ ⎱ atomic ratio Ni/Fe = 2·16
Nickel ...   ... $60·42 \pm 0·05\%$ ⎰
Impurities ... $13·07_4$ (by difference).

With this sample the insoluble residue after treatment with acids amounted to 3·30% of the original weight. This on fusion with potassium bisulphate yielded 0·056% of iron, which is included in the iron content (26·506) given in the above analysis.

There is a marked difference between the amount of iron recovered from the insoluble residue in the two cases. Also the amount of insoluble residue is very different. Since there is such a small amount of residue found in the second sample compared with the first, the figures of the second analysis have been taken as representing the composition of the interior of the specimen more accurately than those of the first analysis, and will be used in calculations that may follow.

8. *Discussion.*

It has been mentioned that on careful examination the spectra in fig. 2 contain lines in addition to those characteristic of a face-centred cubic structure for which the values of $Q^2 [= (h^2 + k^2 + l^2)]$ for the first five lines are 3, 4, 8, 11, and 12. The faint lines were measured and it was found that three fitted the values of $Q^2 = 2$, 5, and 6, but the remaining three did not fit, although they fell near the lines of a simple cube. This suggested a super-lattice, and the point was further investigated.

It was assumed that in each elementary cell there was an atom of oxygen in addition to two atoms of nickel and one atom of iron. Such an assumption might cover the possibility that the alloy dissolved a certain amount of nickel oxide. The suggestion can be checked by calculation of the amount of impurity (assuming it to be mainly serpentine

of density 2·6 gm. per c.c.) in relation to the amount of alloy. The density of the alloy constituted as above works out to be 7·0 gm. per c.c. if the lattice parameter is taken to be 3·5516Å. and the atomic weights of oxygen, iron, and nickel are taken to be 16·0, 55·84, and 58·69 respectively. Taking the density of the original material to be 6·6 gm. per c.c., the ratio of the volume of alloy to the volume of impurity is found to be 10 or the ratio of the masses is 27. But from the chemical analysis the ratio of their masses is 86·926/13·074 = 6·65. The disagreement between these figures is so great that it invalidates the assumption that the super-lattice mentioned exists in the material. The extra lines observed in the spectra must therefore be put down to impurities.

It will next be assumed that the material consists of pure nickel-iron alloy mixed with impurities. Taking the figures from the analysis, and assuming that all the iron and nickel present alloy with each other, then there is present in the alloy 30·49% of iron and 69·51% of nickel by weight, that is, 31·6 atoms of iron to 68·4 atoms of nickel. The ratio of the number of nickel atoms to iron atoms is therefore 2·16.

If the iron found in the insoluble residue (0·056%) be omitted, the atomic ratio Ni:Fe becomes 2·12, which is not appreciably different from the other value. Whichever figure is taken, the ratio agrees better with the formula $FeNi_2$ than with the formula Fe_2Ni_5.

Calculating again, as was done previously, the ratio of the mass of pure alloy to the mass of the impurities, but in this case taking the density of the alloy to be 8·5 grams per c.c. (calculated on the basis of the parameter value 3·5516Å. and a ratio of two atoms of nickel to one of iron), it becomes 6·5 against 6·6 found by chemical analysis. The agreement here is remarkably good, and lends support to the view that the material consists of a mixture of nickel-iron alloy and an impurity which is assumed to be serpentine.

Another view may be put forward. If it be assumed that the natural alloy consists only of iron and nickel with no impurities entering the lattice, then from the parameter-composition curve[1] obtained with alloys artificially prepared from pure nickel and iron, a parameter of 3·5516Å. corresponds with a composition of 70·9 atomic % nickel, which makes the atomic ratio Ni:Fe = 2·44. This figure is nearer 2·5 than 2·0, agreeing more closely with the formula Fe_2Ni_5 than with the formula $FeNi_2$.

There is no direct means of deciding definitely between these two contradictory results. The assumption that no impurity enters the

[1] See E. A. Owen, E. L. Yates, and A. H. Sully, Proc. Physical Soc., 1937, vol. 49, p. 315.

lattice of the natural alloy is, however, unlikely to be true, especially as cobalt and copper are usually found in small quantities in these minerals. The lattice parameter of a pure nickel-iron alloy containing 68·4 atomic % nickel is 3·5550Å. The lattice parameter of the natural alloy (3·5516Å.) is therefore slightly smaller than that of an artificial alloy of the same composition; the difference in parameter is 0·0034Å., corresponding to a difference in density of about 0·02$_5$ or 0·3%. A slight amount of impurity, if it entered the lattice, might account for this difference. It is probably safer in this instance to accept the conclusions reached from chemical analysis than from measurements of lattice parameter, although neither course is free from objection.

9. *Conclusions.*

(1) The mineral 'awaruite' from Grant's Pass, Josephine County, Oregon, consists of a mixture of nickel-iron alloy with impurities, the chief of which is probably serpentine.

(2) Chemical analysis shows the mineral to contain 26·50% of iron, 60·42% of nickel, and 13·07% of impurity. (Deducting impurities, 30·49% Fe, 69·51% Ni.) The ratio of the number of nickel to the number of iron atoms present in the mineral is 2·16.

(3) This mineral has a density of 6·6 grams per c.c., the density of the nickel-iron alloy alone being 8·5 grams per c.c.

(4) The mineral contains thirty times its own volume of gas made up of a mixture of hydrogen and carbon monoxide in equal proportions. The gas is discharged at all temperatures up to 900° C., but the rate of discharge reaches a maximum at about 400° C.

(5) The nickel-iron alloy possesses a face-centred cubic structure, the lattice parameter of which is 3·5516Å. The lattice parameter of an artificially prepared alloy of the same composition is 3·5550Å.

(6) The investigation does not definitely decide whether the alloy conforms to the formula $FeNi_2$ or to the formula Fe_2Ni_5. Certain considerations point to the former as being the more probable.

10. *Acknowledgements.*