

O T T A W A

March 20th, 1942.

R E P O R T

of the

ORE DRESSING AND METALLURGICAL LABORATORIES.

Investigation No. 1183.

Examination of Copper-Nickel Alloy
Strip and Bullet Envelopes.

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(Copy No. 15.)

BUREAU OF MINES
DIVISION OF METALLIC MINERALS
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ORE DRESSING AND
METALLURGICAL LABORATORIES



CANADA
DEPARTMENT
OF
MINES AND RESOURCES
MINES AND GEOLOGY BRANCH

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Origin of Problem and Object of Investigation:

In February, 1942, Lt.-Col. F. C. D. Tothill, of the Inspection Board of the United Kingdom and Canada, Ottawa, Ontario, reported verbally that tracer ammunition and a few rounds of ball ammunition had been giving trouble owing to the cracking of the copper-nickel bullet envelopes. He also stated that Anaconda American Brass Limited, the

(Origin of Problem and Object of Investigation, cont'd) -

suppliers of the copper-nickel alloy, have reported that probably Nickel-Silver (copper-nickel-zinc alloy) had been added by mistake to these copper-nickel alloy lots, and it was claimed that this is probably the reason for the defective results given by this material.

Lt.-Col. Tothill requested an examination of that material in order to determine whether the physical properties were seriously impaired by zinc additions.

Table I gives information on the samples submitted.

Strips marked Nos. 1, 2, 15 and 16 were submitted as samples of stock being used in the plant of Defence Industries Limited, at Brownsburg, Quebec. The submitted defective bullet envelopes showed numerous cracks on the bearing surface, especially pronounced on the depressed areas caused by the rifling.

Strips numbered X8, X16, and X38 were made especially by Anaconda American Brass Limited, New Toronto, Ontario, to check the influence of zinc content on the performance of the copper-nickel used for bullet envelopes.

(Table I follows on next page)

TABLE I.

<u>Date</u>	<u>Material</u>	<u>Marks</u> [⊙]	<u>Source</u>	<u>Remarks</u>
Feb. 7, 1942	Strips	No. 1. No. 2.	Defence Industries Ltd., Brownsburg, Quebec.	No accompanying information.
Feb. 9, 1942	Bullet	(A)	Defence Industries Ltd., Montreal, Quebec.	.303 tracer bullet (fired).
Feb. 9, 1942	Bullet Envelope	(B)	I. B. U. K. & C., Washington, D.C.	Ball ammunition (fired).
Feb. 12, 1942	Strips	{ No. 15	Defence Industries Ltd., Brownsburg, Quebec.	Sample of lot giving erratic bullet jackets.
		{ No. 16	Defence Industries Ltd., Brownsburg, Quebec.	Sample of lot tested and found zinc-free.
Feb. 28, 1942	Strips	No. 3 (X38)	Submitted by Anaconda American Brass Ltd., New Toronto, Ont., to I.B.U.K. & C., Ottawa, Ontario.	Approx. .20 - .25% Zn.
		No. 16 (X16)		Approx. over 1% Zn.
		No. 38 (X38)		Showed no evidence of Zn.

⊙ The distinguishing marks on the submitted samples are given; those given in brackets are marks given in these laboratories to prevent confusion.

(Origin of Problem and Object of Investigation, cont'd) -

Similar material was investigated by the Anaconda American Brass Limited and the results were reported to Lt.-Col. Tothill who forwarded them to these laboratories by letter on February 24th, 1942, and requested an opinion. The conclusions reached in their investigations are that zinc additions are not responsible for erratic behaviour of the copper-nickel alloy bullet envelopes. However, they found lead content, higher than usual, in the unsatisfactory samples and considered that this might be the probable cause of the trouble.

They stated their belief to be that failure was due to heat-cracking from high temperature caused by friction of the bullet in the gun barrel and in the air plus that from the ignition of the smoke compound. This behaviour, in the opinion of the Anaconda American Brass Limited, is the expected result of high lead in the metal.

In a letter dated February 27th, 1942, information was given to Lt.-Col. Tothill regarding the chemical analysis obtained on the samples submitted up to that date. In this examination no lead was detected, but in Lot No. 15, which gave erratic results, excessive amounts of sulphur, iron, and carbon were found, which probably caused the "hot-shortness" of the material.

However, the probability of lead being present although not detected was considered a possibility. In order to ascertain whether any lead was actually present, especially large samples, taken from Strips Nos. 15 and 16, were again analysed for this element. The revised results are given in Table II, showing that in Strip No. 15 the lead content was 0.044 per cent but that in Strip No. 16 no lead was found.

Chemical Analysis:

Table II gives the results of the chemical analysis on all submitted samples. Due to the small amount of bullet jacket material available, complete chemical analyses could not be made.

All chemical analyses were checked by qualitative spectrographic examination, with the exception of carbon and sulphur.

Mechanical Properties:

Tensile Tests -

Table III shows the results obtained on standard-sized test pieces with the exception of Samples Nos. 1 and 2, the lengths of which did not permit the determination of the proof stress.

All test pieces were cut in the longitudinal direction and the tests were carried out at room temperature.

Hardness -

Hardness was determined by the Vickers method, using a 10-kilogram load. The results are given in Table III.

(Tables II and III
appear on following
pages.)

TABLE II.

RESULTS OF CHEMICAL ANALYSIS.

Sample No.:	-(Per cent)-							Bullet Jackets	
	1	2	15	16	X8	X16	X38	A	B
Copper	84.63	84.77	84.22	84.86	84.74	84.00	84.81		
Nickel	15.28	14.98	15.14	15.08	14.78	14.60	14.98		
Manganese	0.16	0.14	0.28	0.15	0.17	0.16	0.17		
Zinc	None	None	None	None	0.15	1.21	None	None	None
Lead [⊗]	None	None	<u>0.044</u>	None	0.020	0.010	0.0005		
Iron	0.06	0.19	<u>0.40</u>	0.04	0.09	0.08	0.007	0.08	0.05
Sulphur	None	0.003	<u>0.029</u>	0.005	0.005	0.004	None		
Carbon	0.005	0.010	<u>0.015</u>	0.005	0.009	0.013	0.009		
Phosphorus	-	-	Trace	Trace	Trace	0.003	Trace		
Tin	None	None	None	None	None	None	None		
Silicon	None	None	None	None	None	None	None		

⊗ Lead content in Strips Nos. 1 and 2 was determined only on small samples (1g), due to small amount of material available for this purpose.

(NOTE: "None" signifies none detected.)

TABLE III.

RESULTS OF TENSILE TESTS.

Strip No.	Size of sample, inches	0.1% Proof stress, p.s.i.	Ultimate tensile strength, p.s.i..	Elongation in 2 inches, per cent	Hardness, V.H.N.
1	.044 x .500	-	41,400	45	68
2	.0435 x .500	-	43,000	42	72
15	.044 x .500	19,700	47,500	38	75
16	.042 x .501	21,300	43,600	38	78
X 8	.041 x .498	18,500	44,000	40	69
X16	.041 x .500	20,500	45,900	37.5	77
X38	.0415 x .499	20,100	43,000	40	75

Micro-Examination:

Micro-examination of the submitted samples showed no marked differences in the structure.

Discussion of Results:

The chemical analysis of Strip No. 15, the only sample received of a lot which gave erratic bullet envelopes, shows a considerable amount of impurities, such as sulphur, lead, iron and carbon, much higher than in all the other samples.

Determination of sulphur and carbon content in the submitted defective bullet jackets was impossible due to small amount of metal. These elements are also impossible to detect by spectrographic analysis. The iron content was rather low.

No zinc was found in any of the samples submitted by the Brownsburg Plant of the Defence Industries Limited (Samples Nos. 1, 2, 15, 16). The lead content was found low, except in Strip No. 15.

The chemical analysis of Samples Nos. X8, X16 and X38, taken from strips made especially to check the influence of zinc content on the performance of the bullet envelopes, conform roughly to the analysis given by Anaconda American Brass Limited.

The results of the chemical analysis, given in Table II, do not conform with those reported by the Anaconda Waterbury Laboratory provided that the samples submitted were taken from identical strips.

From the standpoint of mechanical properties at room temperature and microstructure the materials of the submitted strips are very similar.

References from the Literature:

The following abstracts from the literature concerning the problem of heat-cracking of copper-nickel alloys may be of interest:

1. E. O. Jones and E. Whitehead - "The Cracking of Nickel-Silvers in the Course of Annealing." - Trans. A.I.M.E. 73, 1926, 834-849.

"Other causes of increased tendency to crack are:

(1) Impure metal, especially where there is much impurity in the form of inclusions of oxides, slag, graphite, lead, tin-bearing constituents, etc. Quite apart from chemical composition in the ordinary sense, 'dirty' metal due to casting conditions is very likely to crack....."

Discussion of this Paper:-

W. B. Price, Waterbury, Conn. "... A proper correlation of the rolling and annealing schedule will rectify the trouble without special low-temperature annealing to relieve the internal strains. There are zones of compression and non-compression in nickel-silver, depending on the amount of reduction, and the rate at which this metal expands or contracts on heating or cooling is governed by these zones. Fire-cracking in the manufacture of sheet material tubes and manufactured articles is the result of insufficient reduction of the metal."

2. G. R. Draper - "Nickel Silver. The Effects of Some Minor Constituents." Metal Industry, London, 58, No. 22, May 30, 1941, 462-466.

"Lead... As would be expected, lead-bearing alloys are not suitable for plastic deformation, the presence of globules of lead causing severe embrittlement. So great is the effect of lead that material for severe cold working is seldom allowed to contain more than 0.05 per cent Pb. It was observed that, in alloys intended for working,

(References from the Literature, cont'd) -

crystal growth is somewhat retarded by the presence of lead which increased the tendency to fire and water cracking."

"Sulphur even in the smallest quantities is an objectionable impurity producing great brittleness. Nickel-sulphide forms a eutectic with nickel, at 21.5 per cent sulphur, which melts at 644° C. and therefore remains liquid for some time after the mass of Nickel-Silver has solidified. It appears that the solubility of this compound in nickel is extremely small and, when present, it takes the form of films partially or completely surrounding the grains of metal. Being a most brittle compound, its presence is extremely deleterious."

"Carbon. - In the case of wrought alloys the main trouble seems to be that of brittleness due to graphitization. As early as 1919, Thompson⁶ pointed out that graphite might separate out on annealing nickel-silvers containing carbon, and a photomicrograph showed that the free carbon precipitated round the crystals, the resulting material being extremely brittle. This investigator had already shown that the same phenomenon accompanied the annealing of cupro-nickel at temperatures above 700° C. as a result of the decomposition of nickel-carbide, Ni_3C , and it is probable that the same mechanism occurs in the case of nickel-silver. The process of graphitization in all these alloys commenced at the surface and then passed inwards. This was explained by the fact that the formation of graphite involves a distinct increase of volume, and it was only to be expected that precipitation of

⁶ F. C. Thompson, J. Inst. Met., 1919, 22, 327.

(References from the Literature, cont'd) -

carbon should occur first at the surface where this increase could most easily take place.

"Mishima^① found that in the nickel-copper alloys containing carbon the carbon and nickel-carbon solution form a eutectic at 2.20 per cent carbon and 1316° C. By cold rolling nickel-copper alloys with 10, 20 and 30 per cent nickel and containing from 0.01 to 0.086 per cent carbon and annealing at various temperatures between 300° C. and 970° C., it was established that brittleness occurs at 700° C., due to precipitation of graphite at the grain boundaries. Below 650° C. this brittleness does not occur."

"Iron. - From many sources it is agreed that iron hardens the alloy considerably and promotes cracking during cold rolling if present in quantity above 0.05 per cent."

3. B. K. Bose - "The effect of Manganese on the 'Annealing Brittleness' of Cupro-Nickels." - J. Inst. Metals, 60, 1937, 133-141.

"The phenomenon of 'annealing brittleness' in certain nickel-copper alloys has long been observed, and attempts have been made from time to time to explain it and to discover the best remedy. It is now accepted that the cause of this peculiar behaviour lies in the fact that nickel absorbs a considerable amount of carbon, which under certain conditions separates out in such a manner as to cause brittleness. F. C. Thompson and W. R. Barclay^② showed that this brittleness was due to precipitation of free carbon at the grain boundaries, forming an intercrystalline network, which took place on annealing within a certain range of temperatures. A total carbon

^① K. Mishima, World Engineering Congress, Tokyo, 1929, Paper No. 716.

^② F. C. Thompson and W. R. Barclay, J. Soc. Chem. Ind., 1919, 38, 1307.

(References from the Literature, cont'd) -

content of less than 0.04 per cent was found to be rarely harmful.

This brittleness appears in the cupro-nickel alloys only when they are annealed at a temperature above 700° C., and reaches a maximum about 800° C., provided, of course, that there is present in the alloy a certain minimum percentage of total carbon."

4. C. Blazey - Correspondence on the paper by B. K. Bose (above)
- Monthly Journal, Inst. Metals, 4, part 8,
August 1937, 442.

The embrittlement of cold-rolled strip coincided with graphite precipitation, being a function of total carbon content, time and temperature of annealing, and another factor attributed to impurities other than carbon. Failure at all annealing temperatures occurred at a graphite content of 0.005 per cent, further precipitation leading to no improvement in ductility.

Conclusions:

1. The cracking of copper-nickel bullet envelopes in service was caused by "hot-shortness".
2. As stated in many references in the literature, some of which are given in this report, this "hot-shortness" is caused by higher amounts of impurities, especially by sulphur, lead, carbon and iron. This statement is confirmed by the results of the chemical analysis of Strip No. 15, the only one which was reported to have given erratic results.

(Continued on next page)

(Conclusions, cont'd) -

3. Probably the excessive amount of sulphur, possibly aggravated by higher contents of lead, iron and carbon, is the contributing factor of the defects.

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