D. F. Rendle, [1] *Ph.D.*

Analysis of Brass by X-Ray Powder Diffraction

ABSTRACT: X-ray powder diffraction provides useful discrimination between brass specimens that occur as contact traces. Phases are identified and under favorable circumstances may be quantified. The copper/zinc ratio within a single-phase brass can be estimated with ease to $\pm 1\%$.

X-ray powder diffraction (XRD) is an extremely versatile, nondestructive instrumental method of analysis. It can be used for the analysis of widely differing polycrystalline materials ranging from organic compounds containing light elements carbon, hydrogen, nitrogen, and oxygen through inorganic salts of metals to heavy metals of high atomic number and their alloys [1]. During the last five years this journal has published papers describing the use of XRD for the analysis of materials such as drugs and their excipients and explosives [2–4]. This paper describes the application of XRD to the analysis of an important alloy, brass.

In this laboratory methods such as X-ray fluorescence, microprobe analysis, and emission spectrography are generally used for qualitative analysis of metals and alloys. Unlike XRD, however, these elemental methods of analysis are incapable of distinguishing between the various crystalline phases that may occur in a metal or alloy. For quantitative analysis, the microprobe and atomic absorption spectroscopy (AAS) are used, and of the two methods the microprobe provides greater accuracy (about $\pm 1\%$) in determining copper and zinc concentrations simply because AAS is intended for trace element analysis and not major element quantitation. Phase identification can also be accomplished by optical metallography; however, optical methods are limited to rather large specimens that are easy to mount, polish, and etch in Perspex® supports. In this laboratory phase analysis by metallography would not be attempted on specimens weighing less than 100 μg if for no other reason than to avoid losing the specimen.[2]

Basic Theory

Figure 1 is a phase diagram of the copper-zinc system. The most commonly encountered brasses are alpha, beta, and alpha/beta or duplex brass. Phases gamma to eta are rarely used commercially on account of their brittleness. Alpha brass is a solid solution of zinc in
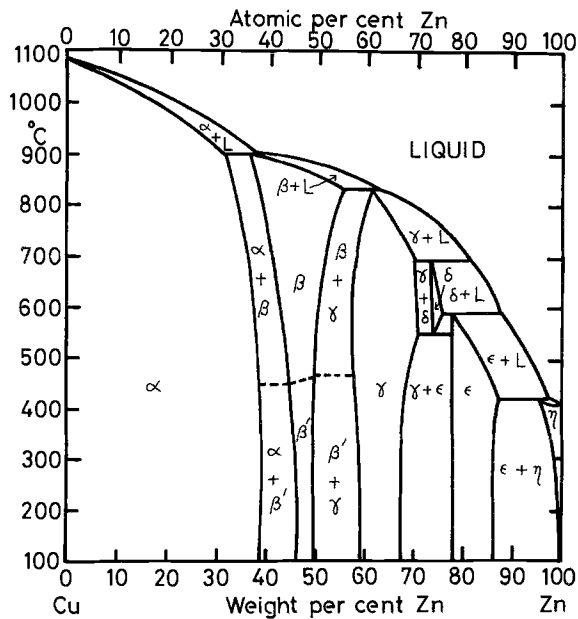
FIG. 1—*The copper-zinc system (after Ref 9, p. 346)*

copper with a maximum range of solid solubility of 0 to 38% (atomic) zinc, while beta brass below 454°C has a maximum range of solid solubility of 46 to 50% (atomic) zinc [5]. Alpha and beta brasses have face-centered-cubic and body-centered-cubic crystal structures, respectively, and consequently can be readily distinguished by their X-ray diffraction patterns. Further discrimination can be achieved by estimation of the copper/zinc ratio within a single-phase alpha brass and by estimation of the alpha/beta ratio in a duplex brass.

Substitution of zinc for copper in the crystal lattice results in lattice expansion, and the most sensitive measure of this expansion is obtained by measurement of diffraction maxima at high (75 to 90°) θ angles [6]. The lattice parameter a of the cubic unit cell is related to the Bragg angle θ_{hkl} by the equation

$$a = \lambda (h^2 + k^2 + l^2)^{1/2} / 2 \sin \theta_{hkl}$$

where λ is the wavelength of radiation and h, k, and l are the Miller indices of a crystal plane. To determine the percentages of copper and zinc in a given alloy, the value of a obtained from that alloy is compared with those values from brasses of known composition.

Experimental Methods

Brasses used in this study were grouped as follows: (a) standards of known composition and (b) specimens obtained from objects in everyday use. Standard brasses were obtained from Metallurgical Services Laboratories Ltd., Betchworth, Surrey, England. Control specimens of brass are obtained in two ways; by cutting with a scalpel to get a small sliver of brass and by using a needle file to get fine filings. In a large percentage of cases, filing an exhibit would not be permitted and a small sliver of brass would have to be removed carefully by scalpel. However, filings are preferable and are used whenever possible in case

work. Filings no larger than those which pass through a 63-μm sieve are used in case work specimen analysis and were used for the purposes of this study. Individual slivers weighing 20 to 100 μg are suitable for X-ray powder photography. Before the XRD analysis, filings were annealed inside sealed glass tubes at 500°C and slow-cooled to room temperature over 12 to 15 h. The annealed filings were then sealed in thin-walled glass capillary tubes (0.3-mm bore) supplied by Pantak (EMI) Ltd., Windsor, Berkshire, England.

Diffraction patterns were recorded with 114.6-mm-diameter Debye-Scherrer powder cameras. Iron-filtered cobalt Kα radiation ($\lambda = 0.179026$ nm) from Philips' fine-focus X-ray tubes powered at 35 kV and 34 mA was employed for all specimens. Exposures of 1 h were used with Kodak "Kodirex" KD59T film. Diffraction line spacings were measured to 0.05 mm with a hairline cursor equipped with a vernier scale (Charles Supper Co. Inc., Natick, Mass.), and line intensities were measured with a Joyce-Loebl Mark III C double-beam recording microdensitometer. An estimate of film shrinkage was obtained from the spacing determinations. Values of a, the lattice or unit cell parameter, for each brass were calculated from a least-squares fit of observed and estimated θ values weighted according to a scheme developed by Nelson and Riley [7]. A computer program written by Whitlow [8] to perform the weighting and least-squares calculations was used for this work.

Seven standard brasses of known composition and a selection of brasses from twelve objects were analyzed by the methods outlined above.

Results

The first seven photographs in Fig. 2 show Debye-Scherrer powder patterns of brasses of known composition; the final two are included to show the difference in quality of powder patterns produced by a sliver of brass before and after annealing. Figure 3 shows powder patterns of a number of brasses encountered in objects used everyday. Lattice parameters for single-phase alpha brasses of known composition are listed in Table 1 and are plotted in graphical form versus the percentage of zinc in Fig. 4.

Lattice parameters, alpha/beta ratios, copper/zinc ratios, and other phase information for brasses in objects of common occurrence are listed in Table 2.

Film shrinkage in each case was less than 1 in 180 mm (<0.55%).

Discussion

X-ray diffraction patterns of the various phases of brass are shown in two standard texts [9,10] and a limited amount of diffraction data is recorded in the file of the Joint Committee on Powder Diffraction Standards [11], but, with the exception of data published by Rao and Anantharaman [12], little information is available concerning alpha brass lattice parameters.

Consequently, the "standard" films shown in Fig. 2 are useful for comparison purposes when a rapid, approximate estimate of the percentages of copper and zinc in an alpha brass is required. However, when a more precise percentage is required lattice parameters are calculated [7,8] and the results transformed into the percentage of zinc by using the graph shown in Fig. 4.

Figure 2 illustrates the degree of distinction obtainable by XRD methods between alpha, beta, and duplex brasses. Within the alpha brass series (1 to 5), a steady increase in diffraction line spacing (on the right-hand side of the photographs) is noted, concomitant with the increase in zinc content. The powder patterns in Fig. 3 indicate that brass from objects having "working" uses tends to be duplex or an alpha brass with a high (>30%) zinc content, such as the Yale latch, the hinge, the water tap, and the Yale lock cylinder. Items of a decorative nature, such as the light fixture, tend to have alpha brass with higher copper content. It is interesting to note that the latch, retaining ring, and cylinder from one Yale lock
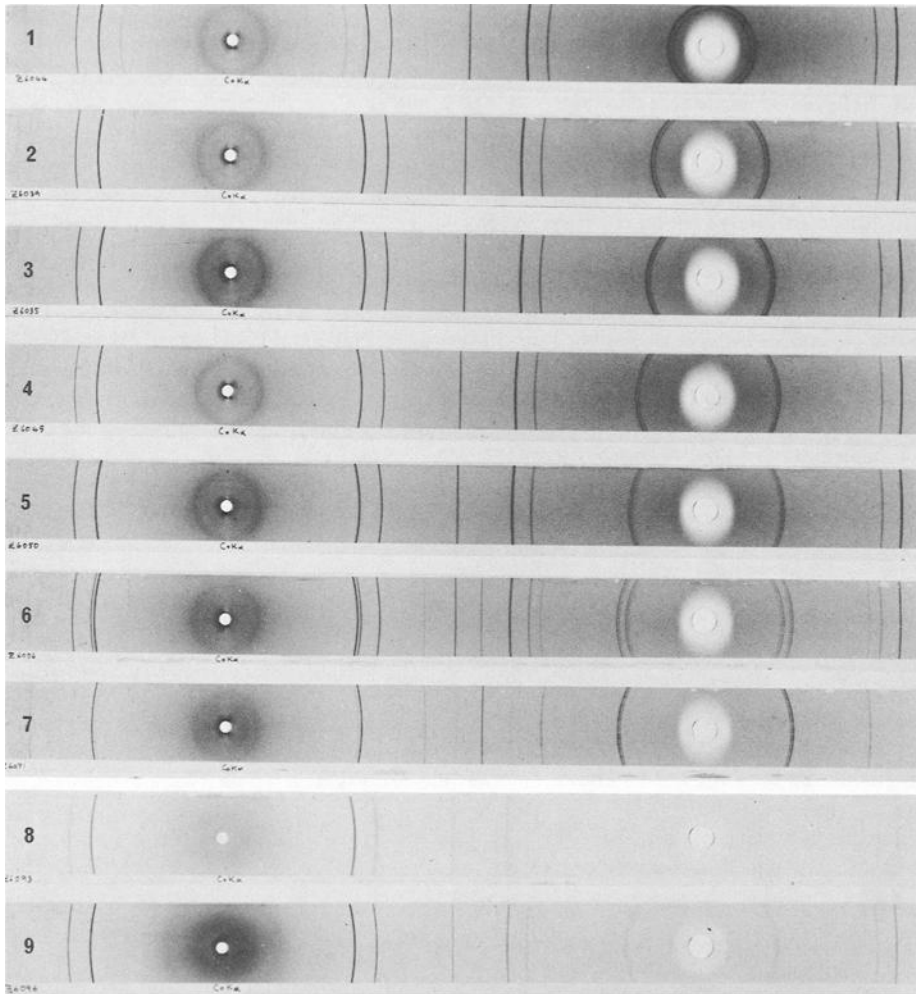
1 Copper with traces of cuprite
2 85/15 alpha brass, some cobalt Kβ lines present
3 80/20 alpha brass, some cobalt Kβ lines present
4 70/30 alpha brass, some cobalt Kβ lines present
5 65/35 alpha brass, some cobalt Kβ lines present
6 60/40 alpha/beta brass (Muntz® metal)
7 50/50 high beta content alpha/beta brass
8 Fake astrolabe (sliver of unannealed specimen)
9 Fake astrolabe (sliver of annealed specimen)

FIG. 2—*Debye-Scherrer powder patterns of brasses.*

are each made of a different brass. Similarly, the original Yale and Chubb keys supplied with their respective locks are made of brasses that differ considerably in composition.

Duplex brasses tend to have lattice parameters that are similar both in alpha and beta phase composition (Table 2) and, with the exception of brazing rod #2, discrimination between them on lattice parameter measurement alone is not feasible. Measurement of the relative intensities of the strongest diffraction lines of alpha {111} and beta {110} phases by
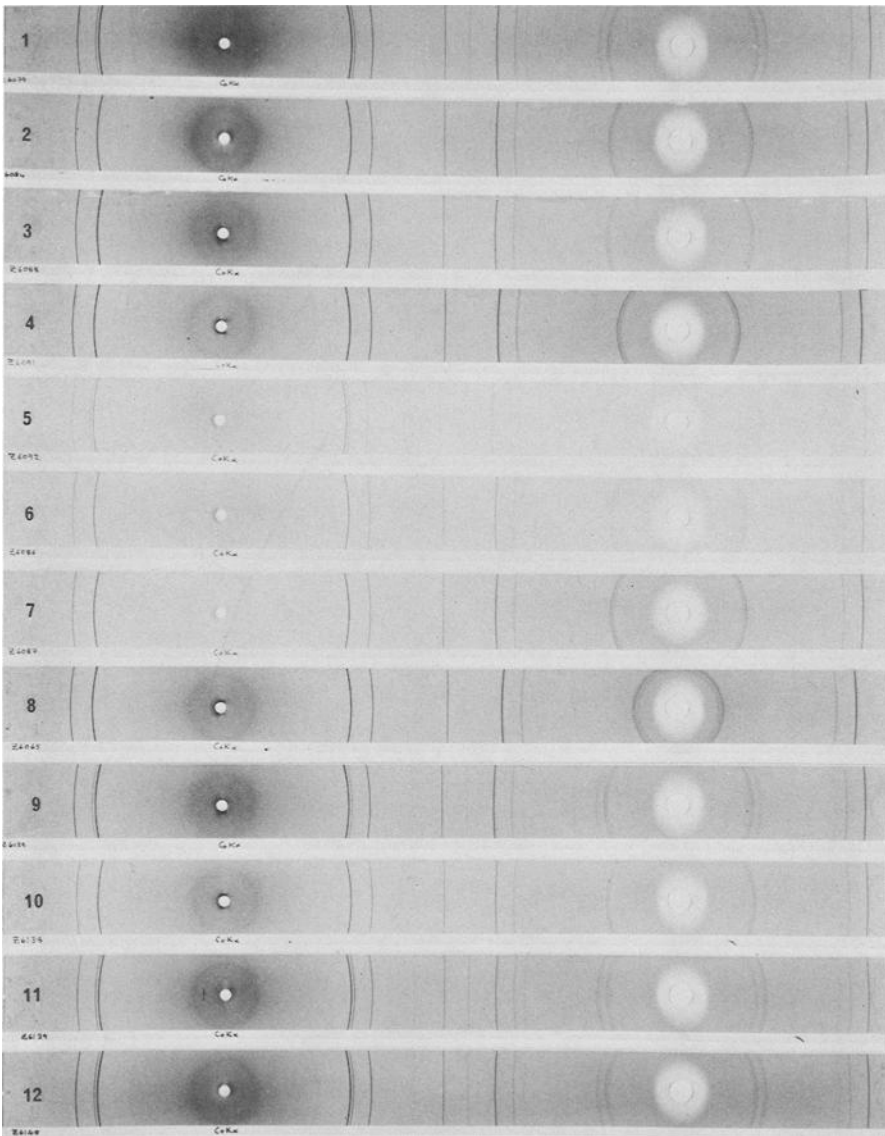
1   Latch from Yale lock
2   Ring from cylinder of Yale lock
3   Yale cylinder
4   Yale key (original supplied with lock)
5   Chubb key (original supplied with lock)
6   .303 cartridge case
7   Bayonet light fixture
8   Brazing rod #1
9   Brazing rod #2
10 Wood screw
11 63.5-mm (2½-in.) cupboard hinge
12 Water tap

FIG. 3—*Debye-Scherrer powder patterns of brass from objects in everyday use.*

TABLE 1—*Lattice parameters of single-phase alpha brasses.*

Film No.	Composition		Lattice Parameter, nm	Standard Deviation, nm
	Copper	Zinc		
1	100	0	0.36148	0.00002
2	85	15	0.36451	0.00003
3	80	20	0.36577	0.00004
4	70	30	0.36800	0.00004
5	65	35	0.36950	0.00004
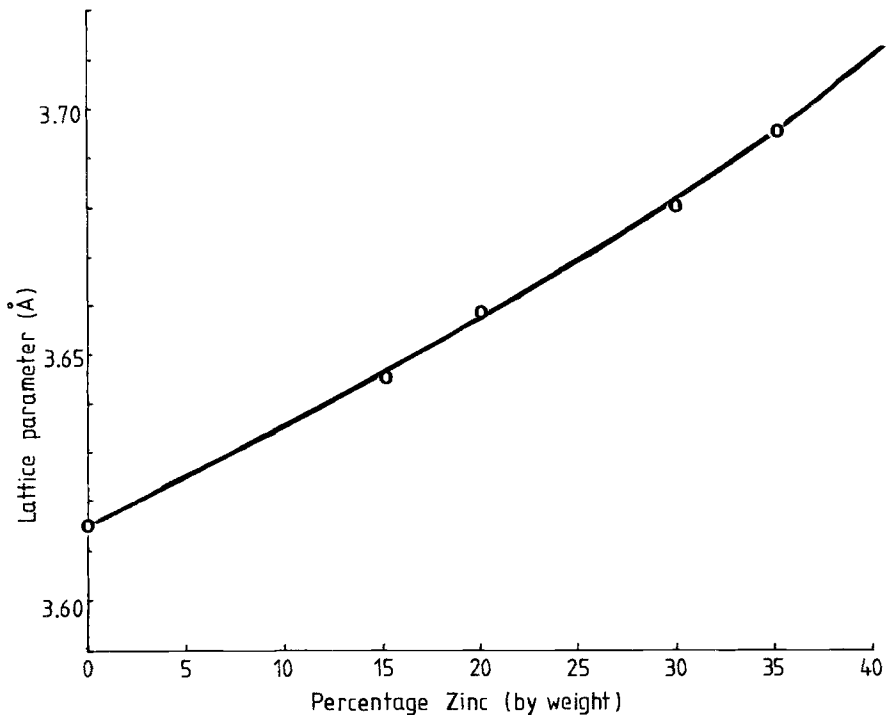
FIG. 4—*Lattice parameter versus percentage of zinc in alpha brasses (1 Å = 0.1 nm).*

microdensitometry yields a ratio and this may well serve as a discriminating factor. The ratios quoted in Table 2 are generally well separated. "Other phases" detected are invariably lead.

The maximum error (or largest standard deviation) in lattice parameter determined for the alpha component of a brass listed in Table 2 is 0.00005 nm, and three times this value (0.00015 nm) represents an error of about 1% in zinc content, according to Fig. 4. Percentages can therefore be quoted as ±1% in copper and zinc content in alpha brasses. Film shrinkage, at less than 1 in 180 mm, is very small and can be ignored since compensation for about 0.5% shrinkage on the diffraction pattern of almost pure copper (Film 1, Fig. 2) results in a lattice parameter of 0.36154(6) nm. The quoted lattice parameter [11] for pure copper is 0.36150 nm, which lies within one standard deviation of this corrected experimental value.

TABLE 2—*Composition of brass from various objects. The alpha/beta ratio in Column 5 is the peak height ratio of diffraction lines {111}(alpha) and {110}(beta).*

Film No.	Object	Lattice Parameter, nm, with Standard Deviation		Alpha/Beta Ratio	For Single-Phase Alpha Brasses		Other Phases
		Alpha	Beta		Copper, %	Zinc, %	
1	latch from Yale lock	0.37016(3)	0.29512(1)	1.69	...	...	lead
2	retaining ring from Yale lock	0.36901(2)	...	...	67.0	33.0	...
3	cylinder from Yale lock	0.36960(1)	...	...	64.5	35.5	possibly very weak beta brass
4	Yale key (original)	0.36593(3)	...	...	79.0	21.0	lead
5	Chubb key (original)	0.37016(2)	0.29513(4)	2.08	...	...	lead
6	.303 cartridge case	0.36797(3)	...	...	70.5	29.5	...
7	bayonet light socket	0.36787(5)	...	...	71.0	29.0	...
8	brazing rod #1	0.36214(2)	...	...	97.0	3.0	...
9	brazing rod #2	0.36991(2)	0.29471(2)	2.15	...	...	...
10	wood screw	0.36979(3)	...	...	64.0	36.0	...
11	63.5-mm (2½-in.) cupboard hinge	0.37012(4)	0.29514(3)	1.98	...	...	lead
12	water tap	0.37017(2)	0.29519(3)	2.30	...	...	lead

Brass is perhaps second only to steel as an alloy in frequency and diversity of usage today [13], which is one very good reason why it occurs frequently as a contact trace in forensic science case work. The two examples given below serve to illustrate the use of XRD for brass analysis in case work.

Case 1

Four men were arrested on suspicion of stealing metal from a junkyard. A quantity of copper cable had been placed in sacks and moved to a point prior to removal by vehicle. Piles of brass and other metals were also in the immediate vicinity. Four pairs of boots, a denim jacket, a sack, and some copper cable were submitted to the laboratory for examination with the request to search the clothing for metallic traces and to compare them with the copper cable. No traces of copper were found but brass swarf was found embedded in the soles of all four pairs of boots.

Control specimens of swarf from the junkyard were compared visually with those removed from the boot soles. A number of differently shaped pieces of swarf were noted, the shape presumably dependent upon the machining process used. Analysis by XRD revealed three distinct types of brass in the swarf: a 65/35 alpha brass, a 70/30 alpha brass, and an alpha/beta brass (about 60/40) with lead. Each suspect was found to have at least two different types of swarf that matched control specimens in shape and composition embedded in the soles of his boots. A direct result of this evidence was the conviction of the four men by the court.

Case 2

A number of old brass navigational instruments purported to be 18th century astrolabes were sold to various antique dealers. Suspicion was aroused concerning their authenticity when instruments supposed to have been made by different craftsmen bore similar engravings. Thorough visual examination suggested that they were indeed fakes, and chemical analyses were undertaken to confirm or refute this suggestion. Analysis by XRD of a sliver of brass weighing about 100 μg removed from an astrolabe revealed a single-phase alpha brass composed of 65% copper and 35% zinc. Since brass of zinc content greater than about 30% was not produced commercially until the 19th century [14], the instrument was obviously made of a modern brass. In addition, analysis by X-ray fluorescence revealed a marked lack of trace elements that would have been present in 18th century brasses.

In general, case work specimens are examined as received initially—resulting in powder photographs such as Type 8 in Fig. 2. If there are obvious differences between control and suspect specimens (for example, one is an alpha brass and the other a duplex brass, or one is leaded and the other not), analysis is terminated. However, if the brasses appear identical at this stage then the specimens are annealed as described and powder photographs are taken again. This adds considerably to the analysis time but it is thought that the return for this effort justifies the time spent.

Summary

X-ray powder photography provides a number of ways of discriminating between brasses:

(1) identification of phases (alpha and beta) and discrimination between single phase and duplex brasses;

(2) estimation of copper/zinc ratio within the alpha phase to $\pm 1\%$;

(3) estimation of alpha/beta ratio in duplex brasses based on diffraction line intensities, though at present this aspect has not been fully explored; and

(4) identification of other phases (especially lead) present in brasses that are otherwise quite similar.

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Address requests for reprints or additional information to
D. F. Rendle, Ph.D.
Metropolitan Police Forensic Science Lab
109 Lambeth Rd.
London, SE1 7LP England