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Usefulness of X-ray diffraction and Raman Spectra for understanding metal alloy microstructure repeatability

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This is a quantitative methodology for checking repeatability in microstructure using X-ray diffraction (XRD) and Raman spectra of aluminium and brass. The crystallinity and microstructure of the aluminium or brass samples are different if their manufacturing sources are different, due to differences in processing methodologies. It was quantitatively estimated from their Raman spectral profile. Aluminium and brass, from the same source and batch, showed more comparable XRD and Raman patterns. This method highlighted extent of uniformity achieved using a certain production method and also suggests scope for improvements. It improves testing repeatability of ferrous and non-ferrous metals and alloy products, using these two techniques alone, rather than using a plethora of analytical testing techniques currently used for a metal manufacturing process.

Keywords: Checking repeatability, Microstructure estimation, Raman spectra, X-Ray Diffraction

1 Introduction

Quality and standardization imply the ability to produce the same material again and again with the same performance and physical parameters. These are generally in the domain of various metrology institutes and their certified reference materials[1]. In metals production, this implies that ideally, their microstructure should be the same in all batches, irrespective of the metal. So, ideally, all manufacturers in principle, are expected to have the same or similar microstructure in order the qualify in the same quality and price bracket. The required testing for that is currently based on several destructive and non-destructive methods. Most of it are finally related to their alloy's microstructure, which is qualitative[2]. Quantification of this, if possible, can lead to better repeatability and standardization. We showed earlier that different sources of the same processed iron-based alloys, stainless steel, steel rebars of different brands have different Raman spectral profiles, even if their X-ray diffraction (XRD) patterns were almost the same. It is thus a consequence of their differences in microstructure. Raman spectra has been used well earlier in identification and segregation of different sources of minerals of the same metal [3,4,5]. Here its usage is being extended a bit more. We had also observed earlier that for ferrous materials like stainless steel and steel rebars of different brands, even within the "same steel grade", with change in brand, there is a perceptible change in their XRD and Raman spectral profile[5]. So, it is possible to segregate different brands based on such data – i.e. their microstructure differences can be implicitly quantified if both XRD and Raman spectral data are used[4,5,6]. Now, it shall be shown here that this methodology of quantifying the alloy microstructure and showing their differences or similarities using XRD and Raman Spectra is equally valid for other non-ferrous alloys like aluminium and brass. In the same batch of aluminium or brass of the same brand, the XRD and Raman spectral profile are similar. Thus, quick microstructure quantification and repeatability checks can be done using data from XRD and Raman spectral profile, instead of using a host of methods currently preferred for most metals and alloys.

2 Materials and Methods

Samples of commercial grade aluminium and brass were randomly collected from commercially available sources in the open market, without any bias. Different manufacturing sources were used to get samples of different brands while for checking the extent of repeatability, samples from a single source were chosen. Sample dimensions /size used were compatible with analytical instruments' sample holder dimensions/size.

The X-ray diffraction (XRD) analysis of our samples was done using a Rigaku Ultima IV Powder X-ray diffractometer having a copper target. It was

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operated at 40 kV and 40 mA. Calibration of the instrument was done using alumina powder BND2001, a certified Indian reference material, before collecting the data[7]. Raman spectra of these samples were recorded using a Renishaw inVia Raman Spectrometer, UK having a laser excitation source of 785 nm, using exposure times of up to 60 or 120 seconds. Such higher exposure times were at times needed to get identifiable peaks. Such Raman spectral peaks were identified using published literature reports on Raman spectral lines of known crystalline phases, as discussed below, and duly cited herein. Detailed background subtraction was done using the Origin7.5 software and the data was obtained in a presentable format after requisite Fast Fourier Transform (FFT) based smoothing and filtering for noise removal.

In our earlier research examples on stainless steel, ferrous alloy and steel rebars[4,5,6] we showed that XRD and Raman spectra results could be used as a quantitative substitute in place of their respective qualitative micrographs and also showed the differences in their micrographs. Hence, here, it was decided to forgo the usage of the corresponding micrographs.

3 Results and Discussion

Five different brands of aluminium samples in sheet form of similar expected usage were chosen initially for observing their XRD and Raman patterns e,g, A1, A2, A3, A4 and A5. In all cases, the XRD peak profiles were correlatible to the JCPDS 04-012-7848 pattern applicable for aluminium. It has a cubic crystalline structure. There were three major observed peaks corresponding to the (111) plane at a 2θ value of about 38.5°, to the (200) plane at a 2θ value of about 44.7°, to the (220) plane at a 2θ value of about 65° and to the (311) plane at a 2θ value of about 77.7° values (Fig. 1). It is seen that the relative intensity profiles of the

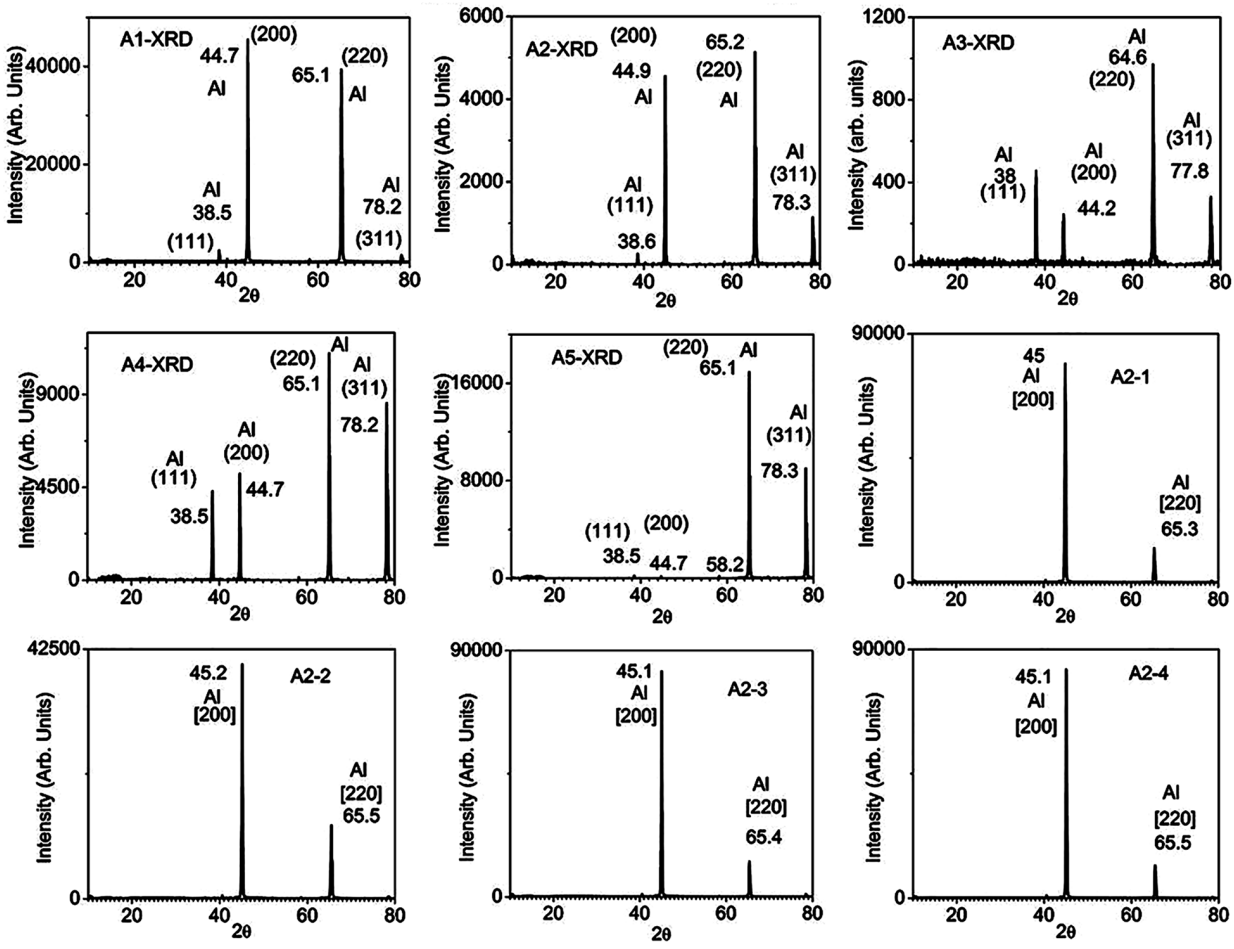

Fig. 1 — Figures marked AX [X=1, 2, 3, 4 or 5] shows the XRD patterns for aluminium samples taken from different manufacturing sources while figures marked A2-Y [Y=1, 2, 3 or 4] shows the XRD patterns for aluminium samples taken from the same manufacturing source and same batch.

different peaks are different in different samples. Moreover, their exact 2θ position and FWHM values also varied a bit from sample to sample as seen in Table 1. XRD spectra from four aluminium samples from the same batch and same make, A2-1, A2-2, A2-3, and A2-4 respectively were now observed. Their 2θ peak values in all cases were at 44^o and 65^o, with no other visible peak. Their relative peak intensity profiles were also much better, almost the same, as compared to the earlier case – i.e. there was a substantial improvement in their crystalline repeatability. However, mathematically speaking, they were not exactly identical (Table 2). The FWHM and relative peak intensity ratios improved significantly within the same batch but there is further scope for improvement.

In order to have an even better understanding of inter-comparison of the micro-structure of the different brands of Aluminium (Al) samples, an inter-comparison of the Raman spectra of these different brands of aluminium samples was also done (Fig. 2). They showed different vibration related peaks at around 270 cm^{-1}, 580 cm^{-1}, 1300 cm^{-1}, 1600 cm^{-1} respectively. Aluminium related Raman spectra peaks have been assigned based on available literature reports[8-11]. The calculated frequency for normal oscillation modes of Al as reported in literature for these ions in aqueous solution is at about 290 cm^{-1} [8]. Higher frequencies were not considered in this reference. In comparison, in Al based alloys, Raman peaks for LA+TA modes are reported at 257 cm^{-1} [9]. The shift observed here is attributable to better purity and differences in crystallineity. In such Al based alloys, A+O Raman peaks were reported at around 565cm^{-1} [9,10,11]. 2O mode related peaks were reported in Al based alloys at around 1325cm^{-1} or at 1523cm^{-1}, depending on the alloying and crystalline conditions[9,10,11]. As compared to an aqueous medium, here the material is not a perfect crystal with an infinitely long periodicity, but molten metal that has been cooled moderately fast. So, there is an element of comparability in these cases. There is another calculated frequency reported at 518cm^{-1}, and at 644cm^{-1} [8]. We have not observed these. Often, due to experimental issues - limitations, our signal quality is a bit noisy. However, no two results or even no two peaks of any two brands were comparable. Ideally, they should have been identical, irrespective of the brand for quality products.

Noise, by definition, in case of electronics or issues associated with signals derived from electronics, is a random disturbance in an electrical signal. It is thermally inherent in any circuitry and can be reduced cryogenically. So, it can be a random disturbance of a useful signal [12,13]. In this case, the signal to noise ratio is perceptible and that is the limitation of the experimental apparatus in this case – we don't have the experimental option to cool the detector to reduce the noise / and improve the signal to noise ratio further. That is the experimental limitation. It is hoped that in future, more advanced instrumentation will be available for this. Signals are specific peaks that are over and above, perceptibly higher than the background noise. In this case, even though there is a perceptible and detectible background noise signal, above that in specific regions, specific peaks are also perceptible beyond doubt, as corroborated by other references available in literature for Raman peaks of the same material aluminium and brass. Hence the peaks detected are indeed peaks in this case, and not noise.

Table 1 — The XRD relative intensities of different peaks in different aluminium samples from different sources

Sample Name	Peak (111) 2θ^o	Relative Intensity (%)	FWHM	Peak (200) 2θ^o	Relative Intensity (%)	FWHM	Peak (220) 2θ^o	Relative Intensity (%)	FWHM
A1	38.5^o	5.5	0.16^o	44.7^o	100	0.17^o	65.1^o	86.2	0.13^o
A2	38.6^o	7	0.18^o	44.9^o	89.8	0.19^o	65.2^o	100	0.16^o
A3	38.0^o	45.7	0.20^o	44.2^o	23.8	0.23^o	64.6^o	100	0.18^o
A3	38.5^o	40.2	0.16^o	44.7^o	48	0.12^o	65.1^o	100	0.11^o
A5	38.5^o	1.4	0.17^o	44.7^o	1	0.18^o	65.1^o	100	0.11^o

Table 2 — The XRD relative intensities of different peaks in different aluminium samples from same batch

Sample Name	Peak (200) 2θ^o	Relative Intensity	FWHM	Peak (220) 2θ^o	Relative Intensity	FWHM
A2-1	45.0^o	100	0.22^o	65.3^o	15.9	0.28^o
A2-2	45.2^o	100	0.20^o	65.5^o	31.7	0.29^o
A2-3	45.1^o	100	0.19^o	65.4^o	15.5	0.26^o
A2-4	45.1^o	100	0.19^o	65.5^o	14.4	0.26^o

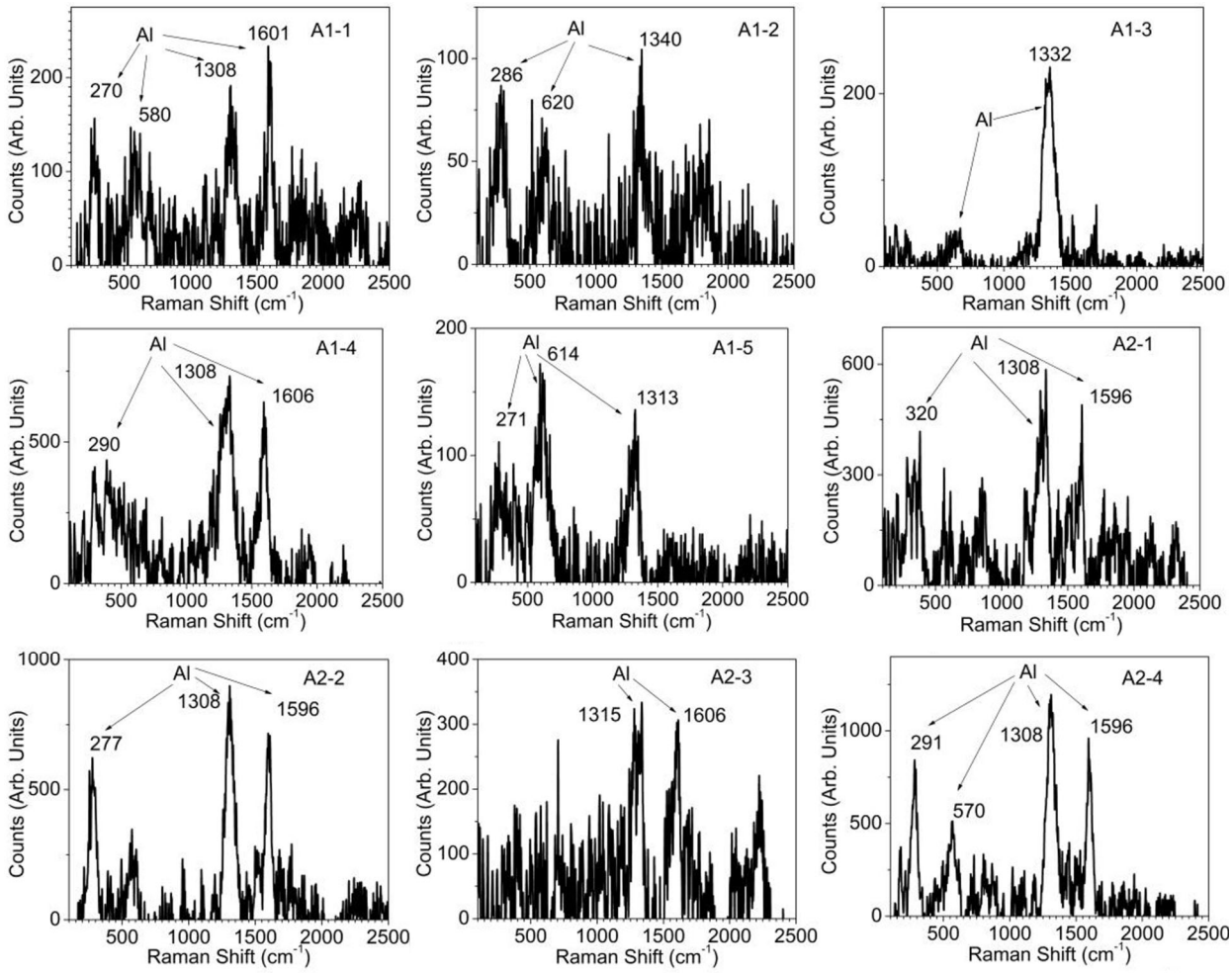

Fig. 2 — Figures marked AX [X=1, 2, 3, 4 or 5] shows the Raman spectral patterns for aluminium samples taken from different manufacturing sources while figures marked A2-Y [Y=1, 2, 3 or 4] shows the Raman spectral patterns for aluminium samples taken from the same manufacturing source and same batch.

Raman spectra is very sensitive to internal defect related stress in the matrix or stress from presence of other impurities. Hence the idea of showing the Raman peak positions and / or their shift is in general to illustrate to the reader the slight changes to situation within the matrix. This was also a reason for considering Raman spectra as a quantitative substitute to represent microstructure for comparisons.

In a perfect single crystal of infinite periodicity, with today's available instrumentation, the Raman spectral peaks are generally high / strong, in the relative sense, as it is an ideal textbook case. In different practical metal and alloy systems, in contrast, one has to largely deal with micro-crystalline and nano-crystalline systems. The very fact that in spite of such differences, Raman peaks are detectable and differentiable, from the noise and from sample to sample having slight crystalline variations is itself a big issue. That is what is being written about here.

Certain mathematical tools (e.g. FFT smoothing) have been used to for smoothing the Raman spectral data, and the noise component, but if these are not judiciously used, peak positions can appear altered.

In contrast, the Raman spectra of aluminium samples from the same batch e.g. samples A2-1, A2-2, A2-3, A2-4 show much better comparable Raman peaks, intensity ratios and related symmetry [Fig.2]. However, the peak positions are not always mathematically identical, but rather comparable. Moreover, some of their lower wave-number peaks are not quite the same too. This suggests there is much more scope for improvement in aluminium's crystalline and microstructure quality and repeatability during production and product shaping. So, different brands of the same material (Al) had different

micro-structures, as shown by their XRD and Raman Spectra, while samples from the same brand and same batch have almost similar spectra, due to better repeatability of samples' metallurgy. So, the corollary question is: - is this phenomenon true for other metals and alloys as well? In that context, another representative alloy, brass, was chosen for a similar study due to its extreme variation in usage prospects.

Figure 3 shows the XRD patterns for Brass samples of different brands but of similar usage e.g. Brass-1, Brass-2, Brass-3, Brass-4 and Brass-5 for a meaningful comparison. All of them are attributable to the JCPDS card number 04-021-1994. The peaks were nominally at 2θ values of 42.4° corresponding to (111) plane, 49.4° corresponding to (200) plane, and 72.5° corresponding to (220) plane respectively. Since the primary constituent of brass is copper, these samples are cubic. However as may be seen from Table 3, the relative peak intensity and FWHM values of peaks of these brass samples are always different. The

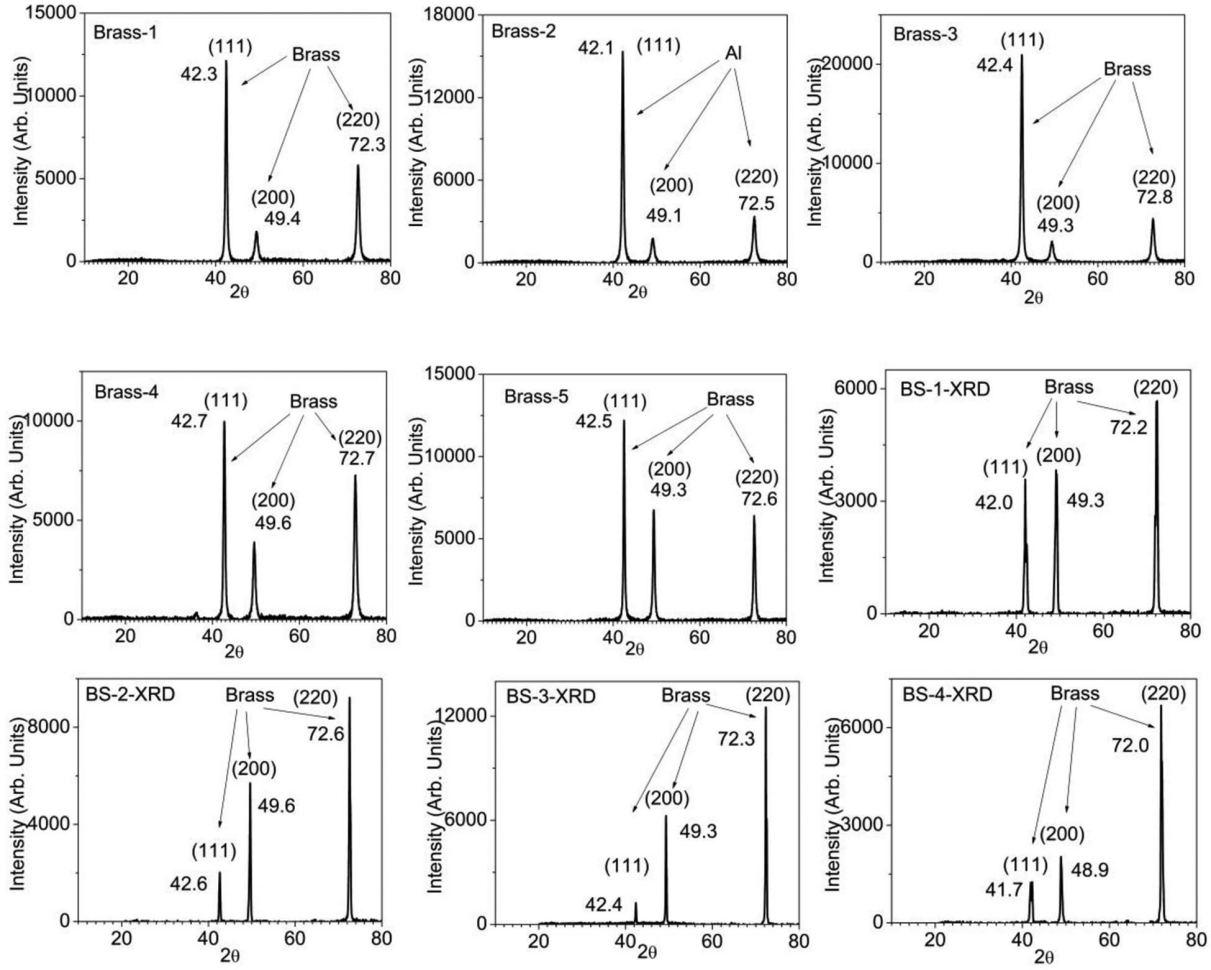

Fig. 3 — Figures marked Brass-M [M=1, 2, 3, 4 or 5] shows the XRD patterns for brass samples taken from different manufacturing sources while figures marked BS-N [N=1, 2, 3 or 4] shows the XRD patterns for brass samples taken from the same manufacturing source and same batch.

Table 3 — The XRD relative intensities of different peaks in different brass samples from different sources

Sample Name	Peak (111) 2θ°	Relative Intensity (%)	FWHM	Peak (200) 2θ°	Relative Intensity (%)	FWHM	Peak (220) 2θ°	Relative Intensity (%)	FWHM
B-1	42.2°	100	0.41°	49.3°	14.5	0.68°	72.6°	47.6	0.61°
B-2	42.2°	100	0.43°	49.1°	11.7	0.70°	72.4°	21.9	0.68°
B-3	42.5°	100	0.44°	49.4°	10.1	0.75°	72.7°	21.6	0.66°
B-4	42.7°	100	0.41°	49.6°	39.5	0.56°	72.9°	72.5	0.57°
B-5	42.5°	100	0.31°	49.4°	55.3	0.40°	72.6°	52.5	0.44°

XRD data of the brass samples of the same batch and make e.g. BS-1, BS-2, BS-3 and BS-4 respectively are also shown in Fig. 3. In relative contrast to the earlier case, most of their peak profiles and relative peak intensities are quite similar and more comparable. The lack of perfect mathematical repeatability of these sample to samples' data is due to the physical variability of these samples due to methodology used for its preparation.

Inter-comparison of the micro-structure of the different brands of brass samples were done using an inter-comparison of the Raman spectra of these different brands of brass samples (Fig. 4). They also showed different vibration related peaks at around 580 cm^{-1}, 1300 cm^{-1}, and 1600 cm^{-1} respectively. The standard Raman peaks as available in various literature and references have been used for assignment of these brass or associated peaks[14-20]. Not so obviously inferred peaks have also been considered and assigned separately[21,22]. The more prominent peak was at around 580cm^{-1} in all cases. The crystalline quality of one of the samples' surfaces (e.g., Brass-1) was poor, leading to noisier data quality, as discussed earlier. Brass-3 had a totally different spectral profile. Thus, no two results or even no two peaks of any two brass brands were comparable. Ideally, they should have been identical, irrespective of the brand if their performances were to be similar.

A comparison of the Raman spectral profile of data from commercially available Brass samples of same make and batch as available in the market, e.g., BS-1, BS-2, BS-3 and BS-4 respectively showed that they generally had peaks at 580-600 cm^{-1}, 1300 cm^{-1}, and a peak at 1600 cm^{-1} respectively. There were slight differences in their exact peak centres possibly due to differences in localized stress levels due to the

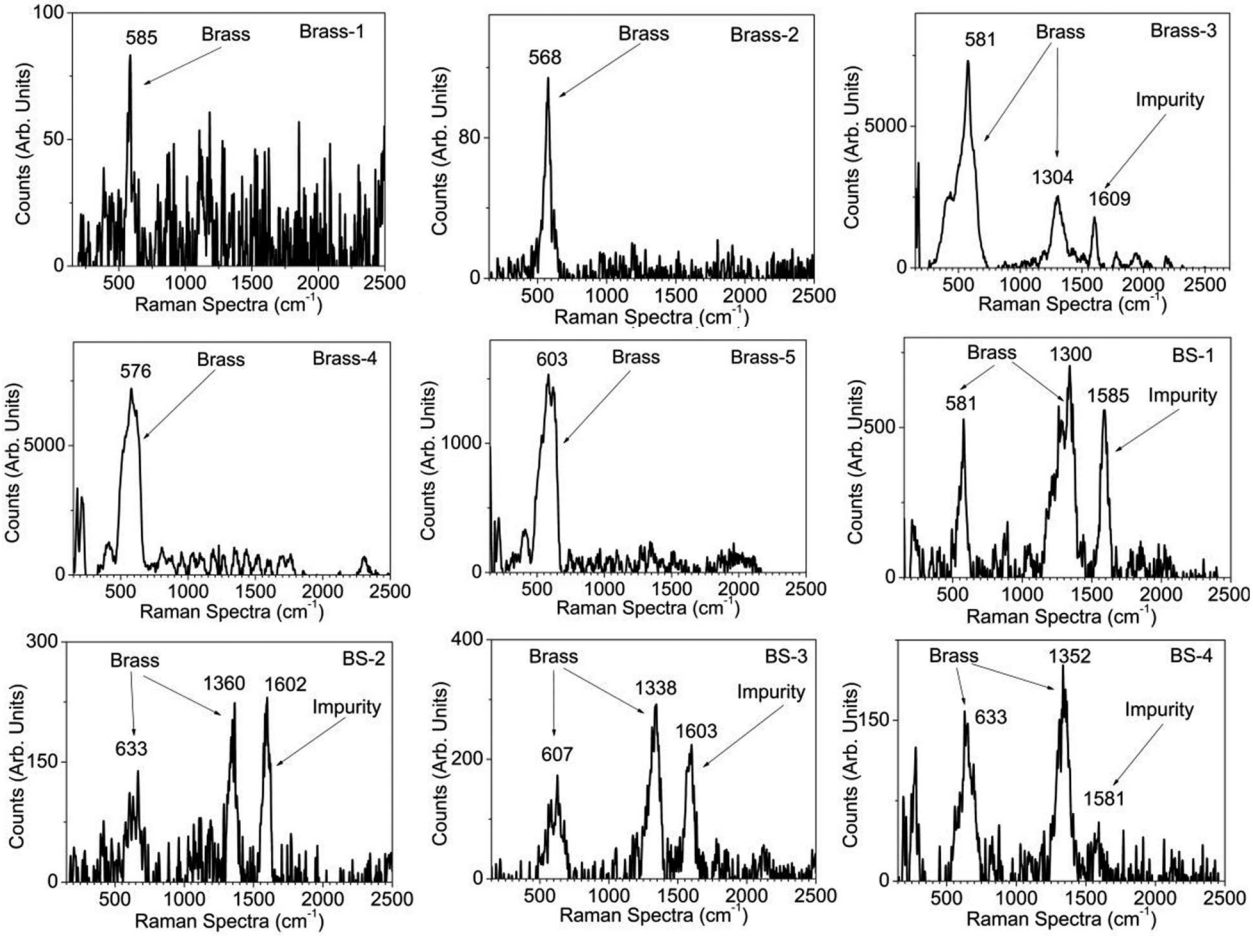

Fig. 4 — Figures marked Brass-M [M=1, 2, 3, 4 or 5] shows the Raman spectral patterns for brass samples taken from different manufacturing sources while figures marked BS-N [N=1, 2, 3 or 4] shows the Raman spectral patterns for brass samples taken from the same manufacturing source and same batch.

Table 4 — The XRD relative intensities of different peaks in different brass samples from same batch and same source

Sample Name	Peak (111) $2\theta^o$	Relative Intensity (%)	FWHM	Peak (200) $2\theta^o$	Relative Intensity (%)	FWHM	Peak (220) $2\theta^o$	Relative Intensity (%)	FWHM
BS-1	42.0^o	62.9	0.4^o	49.3^o	67.1	0.4^o	72.2^o	100	0.4^o
BS-2	42.6^o	22.6	0.3^o	49.6^o	61.5	0.3^o	72.6^o	100	0.3^o
BS-3	42.4^o	09.9	0.2^o	49.3^o	49.6	0.2^o	72.3^o	100	0.2^o
BS-4	41.7^o	18.7	0.4^o	48.9^o	30.5	0.4^o	72.0^o	100	0.4^o

preparation methodology used. The peak at 580-600 cm^{-1} is LO phonon related[14-20]. But peaks in this region can also be attributed to CuO stretching modes[15]. Raman peaks in the range of 1300cm^{-1} and 1600cm^{-1}, similar to the ones observed here, are attributed in literature to presence of carbon and such commonly used starting materials in metallurgy[21,22]. This also suggests that XRD is insufficient to fully detect impurities and defects beyond a certain limit. It also shows the extent of sensitivity of Raman spectra in detecting defects and impurities and distinguishing them in numerical terms. Our methods can suggest the scope and methodology for improving the commercial sample quality as seen in these cases.

So, XRD and Raman spectra of Aluminium and Brass from different brands are different while for the same brand and batch, they are almost the same. There is however, further scope for improvement in production process, uniformity and repeatability in a very general way at every step for their even better performance repeatability. It may also be seen that in the relative sense, if one compares both the XRD and Raman data from the Al samples of same batch and brass samples of same batch, the quality of repeatability of data is a bit more in aluminium than for brass. Brass is being used for hundreds of years, while purification, processing and usage of aluminium is relatively recent. So brass is prepared in a more traditional way while preparation is aluminium is relatively more modern. So, its uniformity and repeatability are a bit better and it is more homogeneous.

A likely reason is that during sheet or any form of preparation, during their required cold rolling or pulling to desired shapes, there is a change of micro-structures in a slight non-uniform way. This is manifested in the observed slight non-identical spectral profile. There is further scope to improve the material quality by repeated and periodic annealing of the samples after each iterative step of shape change to reduce or totally remove such non-uniformity. Hot-rolling and subsequent annealing at each step further improves the situation. But due to economic considerations, often, such manufacturing steps are curtained, with the result that the material quality is often poorer. However, in case of military grade samples, these issues are very often, adequately taken care of, leading to much better quality and better repeatability in their metallurgy.

A feasible protocol for improving such material quality in terms of their microstructure and their repeatability is by improving extent of repeatability of data using above iterative annealing methods. After XRD results can be checked and made repeatable in terms of XRD peak positions, relative peak height ratios and peak FWHM values, efforts at improving the process parameters can be made to improve repeatability of their Raman spectral data as well, in terms of peak position, relative peak heights and subsequently their FWHM values as well.

4 Conclusion

Using aluminium and brass as two sets of representative examples, it was shown here that different makes / brands of a metal show different crystalline planes as prominent peaks in XRD and they also showed different Raman peaks, depending on their crystalline, impurity and defect content differences. If these samples were of the same make and batch, such XRD and Raman peaks were much more comparable. Raman spectra was being used here as a quantitative number for the metal microstructure. So, in aluminium and brass based metals and alloys in general, XRD and Raman spectral data can be used in itself to test repeatability of crystalline phase and microstructure in a quantitative way. This is likely to lead to better quality using faster tests for repeatability, as against a host of methods currently used.

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