A Methodology to Inter-Compare Brass and Such Alloys Manufactured at Different Geographical Locations

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This paper is about a method developed to normalize the Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) data counts of each constituent ion in a mass spectra, by dividing each ion count with the total ion count. So by comparing their statistical means, data of different samples of any alloy like brass *etc.* from different places around the world can be inter-compared using TOF-SIMS data collected using similar separate instruments under similar experimental conditions. Such a methodology can also be extended to analysis of constituents of other materials using TOF-SIMS as well. Here, all brass samples were chosen on a representative global basis and had similar end uses. Variations in normalized mean counts of major constituent ions suggest that brass produced in different parts of the world for similar uses can be a little different in composition and can be readily identified and distinguished using their normalized statistical mean ion counts using TOF-SIMS. Their performance does not drastically change due to variation in such constituents of the alloy as the thermal treatments used on them were possibly different. Based on these observations, it was felt that unless there is a drastic change in any alloys' micro-structure or crystalline phase properties, there will be no drastic change in its properties with variation of its' major or minor alloying constituents. Data from literature using different aluminum alloys as a representative example and using their available data on micro-hardness and noting their variation with alloying also suggests such a phenomena.

Key words: TOF-SIMS, Method for data normalization, Inter-comparison, Alloys

1 Introduction

Metallurgists say that the properties of metal alloys and their performance are dependent on the major and minor impurity profile. It is the impurity distribution of certain elements within the micro-structure that gives rise to the observed strength and properties[1]. If this theory is true, then it must be true for all the different metal alloy systems known and analyzed well. Thus it is imperative to have a look at the impurity distribution inside representative alloys and see how its content variation affects their performance. The most well-known and studied metal alloy systems are brass and different steels, while aluminum, titanium alloys were developed in the last few hundred years *etc*. All of these cannot be analyzed in detail and reported here. So brass was chosen for analysis of its known major constituent and a few representative minor constituents. The number of major or minor constituents chosen are only representative in nature. As per need, it could have been increased as per requirements. In case the micro-structure of such alloys has specific features, then these will also get highlighted in terms of the minority constituents and their distribution profile if

analyzed by Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) ion imaging method[2]. Thus, the original premise for this study was that if special surface features were due to such major or minor impurities alone they would be discernible using mass spectra based ion images. Else, it may be concluded that minority impurities do not have a major contribution to change in alloying properties.

Other analytical techniques like X-Ray Fluorescence (XRF) would not serve the purpose here as it is unable to detect the minor constituents below 1% impurity. It is not a surface feature specific technique and requires a standard sample for quantification, while there is no known concept of standard brass till date. In addition, lower masses and chemical ligands are not be detectable by XRF. X-Ray Photo-electron Spectros-copy (XPS) is unable to detect the minor constituents beyond about 0.05% impurity levels. Since the X-Ray spot size is large, the information content on area to area variation of constituents may be lost. Solution chemistry is not surface specific, and it would be much more laborious and more time consuming than even a detailed TOF-SIMS based analysis. Information about local sample in-homogeneity would again be unavailable. Inductively Coupled Plasma Mass Spectra

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(ICPMS) or Gas Chromatography (GC), methods are unsuitable for such alloys as they need gaseous samples. Atomic Absorption Spectroscopy (AAS) is unsuitable for solid samples and for accurate results, the analyst has to know what to look for. So it is unsuitable for unknown or partly unknown samples[3,4]. Time of flight secondary ion mass spectrometry (TOF-SIMS) has very accurate mass / ion resolution, very high mass analysis range, a very good detection limit, though analysis of chemical state determination is not directly possible. TOF-SIMS techniques also offer information on surface features and on impurities at least at parts per million (ppm) low concentration levels and is location specific [2] with spot sizes of up to 120-500 μm.

All alloys and metals have inherent impurities and these are dependent on the corresponding metal extraction and purification processes used. In terms of constituents and methodology used, as all such processes and associated raw materials are not identical, it is possible to identify their source of preparation. In bullion trade, based on their trace impurity content, in this manner gold and silver are distinguished[5]. However, these are precious metals and expenses for their identification are justifiable. In a similar manner, source of origin of other cheaper metals and alloys may also be identifiable from their impurity profile but it requires development of appropriate and more economical methodologies. It has to be sufficiently robust so that its data can be made independent of a particular specific instrument and should be inter comparable with results using similar instruments. TOF-SIMS based analysis may be such a tool[2,6-10]. The advantages of using mass spectral and ion imaging mode in TOF-SIMS are that (a) the image traits can be used to check for correctness of the mass designation and (b) exaction counts for each ion mass is available for readers as evidence. Relative comparison is readily possible in terms of normalized ions' content based on the analysis and calculation methodology discussed here. This proposed methodology of normalized ion counts is to use ion counts for each ion in a TOF-SIMS mass spectra divided by total ion counts. So a set of TOF-SIMS data collected for say 10 minutes and another collected for say 11 minutes can now be compared based on such a normalization process. Such methodology was not possibly reported earlier in published literature[2,6-10]. So TOF-SIMS can be made into possibly one of the best analytical techniques' to

detect and inter-compare unknown solid samples for their constituents and impurity contents, based on data from different instruments as discussed here. Variation in alloying composition can, in principle, lead to changes in physical properties like hardness, Young's modulus, ductility *etc*. But, modulation of crystalline properties by thermal treatments leading to changes in crystallinity *etc*. can also act as a counterweight. So in spite of variation in alloying composition, due to differences in thermal treatments used leading to differences in crystalline properties, the performance of two alloys may be similar.

In this TOF-SIMS based analysis methodology, one also gets a change to reflect on how metal / alloy preparation has possibly evolved independently at different regions of the world and how this has morphed as per local requirement and availability of local raw materials. In UK, which is isolated by the sea, it is based on what local mineralogy was able to offer. In different parts of continental Europe it may not necessarily be the same. In the new world of North America, the European thoughts and different starting raw materials have led to a different mineralogical result. In the old world of South Asia, brass has been used for a few thousand years. So its processes are not the same as others. Our data was analyzed statistically, in terms of variation in each regions' data in terms of their mean, median count and deviation using several samples from each region.

In order to confirm the generality of deductions obtained using brass, published data of a different matrix like aluminum based alloys and their properties were also considered.

2 Experimental

Authentic brass samples manufactured in different geographical regions were collected for this experiment and grouped into categories like Germany, Scandinavian region, United Kingdom (UK), North America (USA) and South Asia. The brass samples (five or more from each region as categorized here) were chosen in each case in such a manner that their end uses were similar, so that all of them would have gone through similar but not identical thermal and physical treatments. They are nominally designated as 80-20 brass.

2.1 Sample Preparation

All samples chosen had flat surfaces on a certain side of the sample which was suitable for TOF-SIMS data collection. The brass pieces were appropriately

cut as per requirement to make them compatible with the sample holder for the measurements in such a manner that their flat surfaces were used for data collection. They were cleaned with 2-Propanol and dried well before mounting onto the sample holder of the instrument. In case the samples were old, their flat surfaces were also rubbed well before these processes to get the shiny flat surface before this step. So before actual data collection, all samples' analysis areas were cleaned adequately to expose the metallic shine. There were no charging issues as these were metal samples. The samples were initially sputter cleaned using the Bi ion source of the instrument before actual data collection at each data collection spot. Experimental data from each sample was collected from at least two or three spots, depending on the dimension of that particular sample and feasibility issues.

2.2 Methodology

TOF-SIMS measurements were done on brass samples as above, with a TOF-SIMS-V-100 instrument made by M/S IONTOF GmbH using a 25 KeV Bi+ ion source. The instrument vacuum conditions at the main analysis chamber were better than 5×10^{-9} mbar on all days of data collection. The extracter cone tip to sample surface distance was 1 mm. At this vacuum level, due to the higher mean free path of molecules and ions, chances of a collision between molecules / ions are close to zero and TOF-SIMS data can be inter-comparable. It is routinely done and is reported[11,12]. The nominal value of the Bi+ ion current used was 1pA. The rastered area for mass spectral data collection was 500×500 μm in each case. TOF-SIMS raw data in the X-Axis denotes the time taken for each of the ions to travel a certain known distance and data in the Y-Axis denotes counts of each such number of ions during that time and these are then plotted together. For each mass spectral data set, mass calibration was performed on the X-axis data to convert the time scale to the mass scale using the Software Surface Lab of M/S ION-TOF GmbH. The mass calibration peaks used were (H+, HH+), C+, CH+, CH_3+, C_2H_3+, C_3H_5+, C_4H_6+, C_5H_9+, C_6H_{11}+, C_7H_{11}+. Calibrations of such instruments were periodically checked using the mass spectra from an electronic grade Si wafer by using known isotope positions of different known elements before actual data collection. Primarily, the data and results of positive mass spectra are discussed here.

The mass spectra were collected for all samples at different spots in each case and after mass calibration as stated above, certain ion mass peaks were marked for further analysis like Cu+, Zn+, Al+, Si+, Cr+, Mn+ Ni+, Pb+, Zr+ as some of these are known to be major constituents and the rest could be considered as minor constituents of brass as per literature[13-16]. The corresponding ion mass peaks and ion images were then considered. In each sample, individual ion counts for each ion as above and total ion counts were obtained. Individual ion counts, when divided by the corresponding total ion counts give the Normalized Ion Counts for that ion in that measurement. This number obtained is now independent of the instrument parameters for that day and thus is inter-comparable with the similar data from other samples. It can now be compared with similar data of similar samples from some other similar instrument with similar experimental conditions. In the present method, the collected normalized data were not directly averaged. Data was collected from different regions of each sample and over several samples from the same origin to the extent feasible. Ion species wise, all such data was then tabulated region wise to get a statistical mean ion count and statistical median ion count number for that region. In this manner, the statistical values of all normalized ion counts were tabulated for a comparative opinion on relative content of major and minor constituents avoiding various instrumental effects. Their statistical mean and statistical median values have been discussed in tabular form along with the consequences. The choice of minor constituents could have included other impurities. The same methodology used here can be extended for these too and will give similar results.

Such SIMS/TOF-SIMS data are sensitive to matrix effects. However, if all samples' surfaces are of the same type, *eg*. if all of them are of the same type of oxide or of the same type of metals, this matrix effect is effectively nullified. As all sample surfaces are of metallic brass, due to usage of TOF-SIMS with very low sputter currents and associated very low sputter related debris, their matrix effects can be ignored[17].

3 Results and Discussions

In dynamic SIMS, in any routine mass spectral analysis, the sputter currents, related measurements and associated ion yields for similar constituents and samples are not always compared quantitatively across different similar dynamic SIMS instruments. In dynamic SIMS, the ion current is about 1000 times more than that in TOF-SIMS. So the sample surface erosion rate is much higher as compared to TOF-

SIMS. Etch cleaning of a sample surface before analysis is relatively easier. But by the time data is collected the sample surface has greatly eroded. After prolonged usage, due to higher ion current and resultant higher amount of sputtering of sample surfaces in dynamic SIMS, the remnant material inside the vacuum chamber can cause some amount of variation in ion yield on a day to day basis. In TOF-SIMS, the instrument has to be run for a longer period to clean the top layer. But the sample surface is largely intact during data collection and the debris inside the vacuum chamber is relatively much less. Thus its contribution may be ignored for any TOF-SIMS analysis. Dynamic SIMS data on the same instrument are usually compared for different samples based on data collected on the same day of operation to avoid differences in instrumental parameters like sputter current, as it uses O or Cs ions, whose currents can vary a little bit on a day to day basis. The other reason for comparing data on the same day is to avoid changes in relative ion yields, which is in turn related to electron affinities, ionization energies and work function of the sample surface material. This can vary on a day to day basis, due to debris sputtered earlier and present as impurity inside the UHV analysis chamber. Such debris and associated matrix effects in a dynamic SIMS will be relatively much higher. For quantification, the ion counts for a sample with known impurity profile called standard sample is compared with an unknown sample's impurity profile for information of impurity content density in the unknown sample. If data of another ion species were to be required later for the same sample, the measurement has to be repeated. Traditionally, such measurements were done by dynamic SIMS for the semiconductor industry and so the standard samples were prepared traditionally by ion implantation[17]. In TOF-SIMS based analysis which evolved later, an attempt has been made to upgrade the analysis methodology.

In the TOF-SIMS based analysis, which evolved subsequently, Bi+ or Bi- ion based ion currents are also not identical in the same instrument on different days of its operation. The Bi ion current of different instruments are thus never identical as well. Moreover, different operators of different TOF-SIMS instruments may be using different pulse widths for the Bi ion source. In recent times, the number of Bi pulses in a cycle has been increased by some researchers to get a better ion yield[18]. In view of all this, development of a methodology was required to standardize and normalize experimental data taken from different instrumental sources and on different dates using TOF-SIMS measurements.

In TOF-SIMS, data of all ions collected are recorded for posterity, irrespective of the experimenters' interest. Such saved raw data, can be analyzed ion component wise *ie* in this case using Cu, Zn, Al, Si, Cr, Mn, Ni, Pb and Zr ions respectively. Since the total ions collected and its individual ion composition will never change, it is felt that this analysis done by normalizing each such ion counts by dividing each ion counts by the total ion counts and then taking their statistical averages over several samples will make different measurements inter-comparable.

The choice of major and minor impurities considered for analysis as above were based on literature reports on their usage and their likely benefits to the alloying process[19-21]. Other elemental ions could have also been added to this result analysis and discussions but that would not have changed the overall patterns of normalized ion distributions observed. There are some non-negligible normalized ion counts corresponding to the mass number for lead. They fall into the category of minority impurities.

Here five groups of representative ion images from representative samples, each corresponding to a geographical zone *ie*. North America, Germany, Scandinavia, United Kingdom (UK) and South Asia are presented. Their samples' ion counts are closer to their statistical median value for that zone. Figure 1 represents such a representative ion image data of a sample from USA. Fig. 2 represents such a representative ion image data of a sample from Germany. Fig. 3 represents such a representative ion image data of a sample from Scandinavia. Fig. 4 represents such a representative ion image data of a sample from UK. Fig. 5 represents such a representative ion image data of a sample from South Asia respectively. It may be seen that each of these ion images are not similar to one another. Their ion counts distribution as shown by their ion image caption suggests that they are unique in their own way in terms of their alloying composition. Their counts were normalized and statistically averaged for quantitative inter-comparison and discussions. Samples from countries in Eastern Europe or Russia or China were not been discussed or grouped here as they are a closed society and access to reliable samples from such regions are difficult.
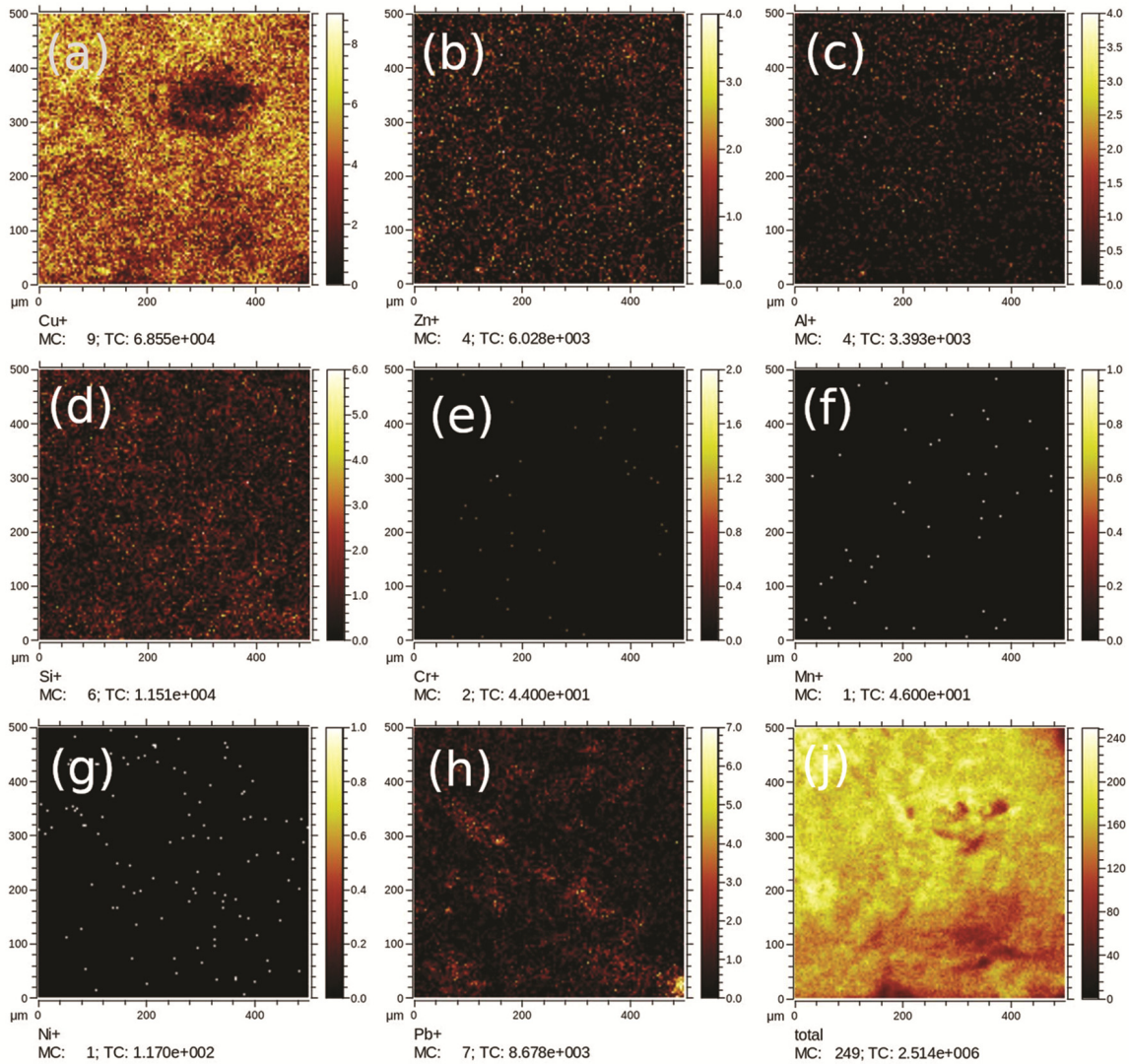
Fig. 1 — Ion image profiles of a representative USA origin brass sample, showing positive ion distribution for (a) Cu, (b) Zn, (c) Al, (d) Si, (e) Cr (low counts), (f) Mn (low counts), (g) Ni, (h) Pb, (i) Zr ions (not shown due to low counts), (j) total ion counts

The normalized and then statistically averaged counts for each ion species chosen as above have been summarized for each group in two tables, Table 1 and Table 2. It was seen that within the same sample, the normalized statistically averaged data from different parts showed the least variation eg. only after the first or second decimal. But within the same geographical grouping of samples, there was an amount of variation leading to a non-zero standard deviation. Based on the data in both the tables, it may be seen that each group of samples are unique in terms of their majority and minority constituents. In fact, adding a few more minority constituents for consideration would not have altered the situation. Samples from different geographical groups are thus discernible by their composition. Any unknown sample can now to be analyzed and compared.

Date of Table 1 or Table 2 shows that the normalized and statistical mean ion counts for the major constituents, Cu and Zn are all most quite the same, for Germany and Scandinavia, both of which are in Continental Europe. That might be expected as they are close by in terms of distance, with similar thought processes involved, information flow and even some raw materials may be common. However, in case of the normalized statistical mean counts for some of the minority ions, the numbers for Germany and Scandinavia are different. Up to major impurities like Al, these numbers seem to still match while the numbers for other minor impurities differ a lot.
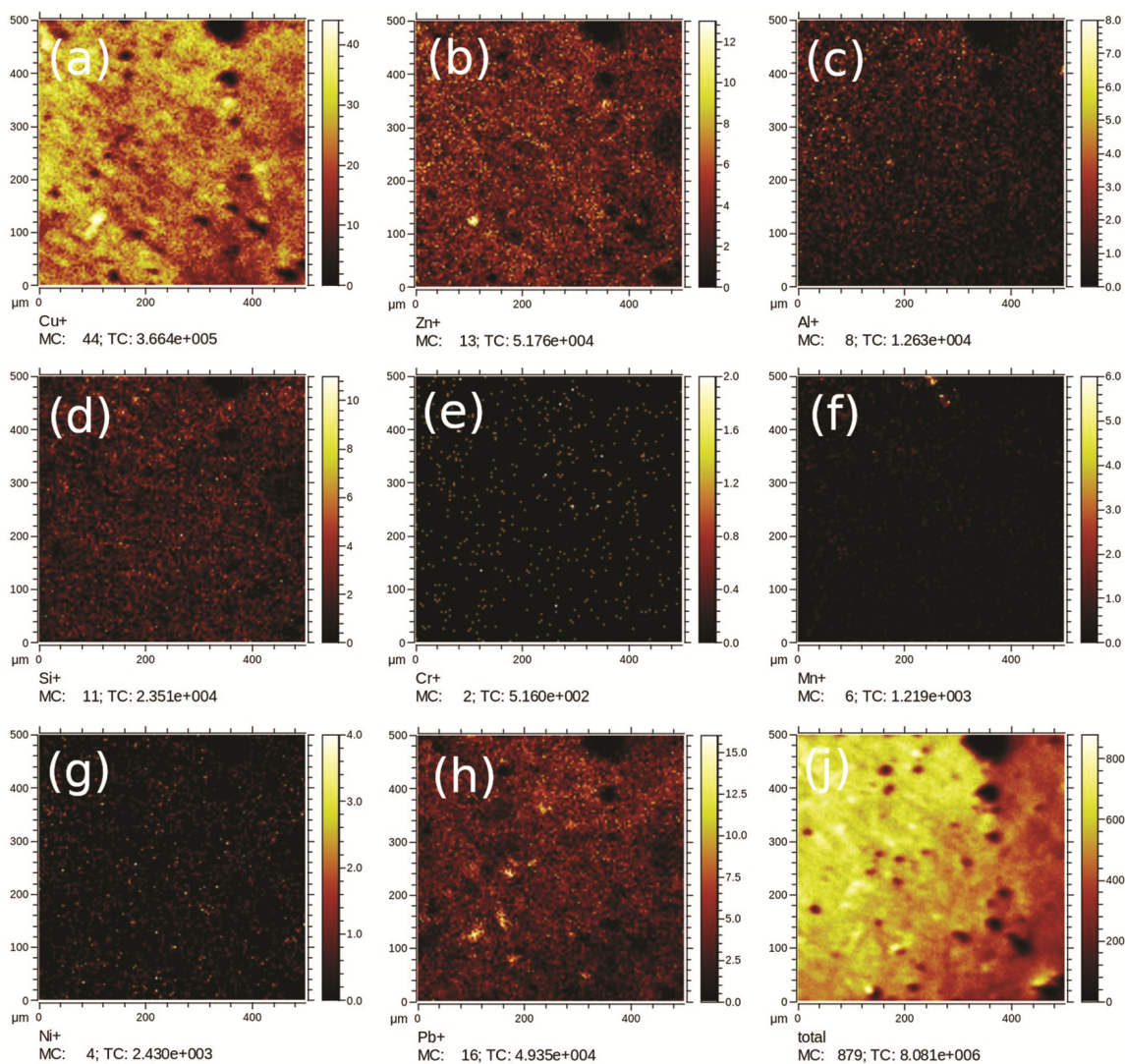
Fig. 2 — Ion image profiles of a representative German brass sample, showing positive ion distribution for (a) Cu, (b) Zn, (c) Al, (d) Si, (e) Cr, (f) Mn, (g) Ni, (h) Pb, (i) Zr ions (not shown due to low counts), (j) total ion counts

Samples from UK showed the highest overall normalized statistical mean counts for Cu and Zn. The statistical mean counts for the other major and minor impurities were proportionately less in these samples from UK. In case of USA, the normalized statistical mean counts for Cu and Zn match closer to that for UK, but their major and minor normalized statistical mean impurity ion counts are much higher than that for UK. In case of South Asian samples, the Cu and Zn normalized statistical mean counts are relatively least among all the samples analyzed but comes closer to the numbers for Germany or Scandinavia. The normalized statistical mean counts for most of the minor impurities are higher for samples from South Asia.

In dynamic SIMS, the ion current is of the order of milli-amperes while in TOF-SIMS, it is of the order of pico-amperes[2,7]. In dynamic SIMS, an exact replica of a surface layer is sputtered in terms of its ions, while in TOF-SIMS, due to reduced ion currents, only a random sample of ions on a surface is sputtered and detected. Hence, in TOF method, theoretically, this might lead to over sampling of a particular ion species or under sampling of a particular ion species due to the random sampling methodology used. In order to avoid such a scenario, during TOF-SIMS based data collection, the algorithms for true randomness are used and sufficient time is allowed for data collection of all the ions to get data truly representative of the analysis area. The statistical mean and median values
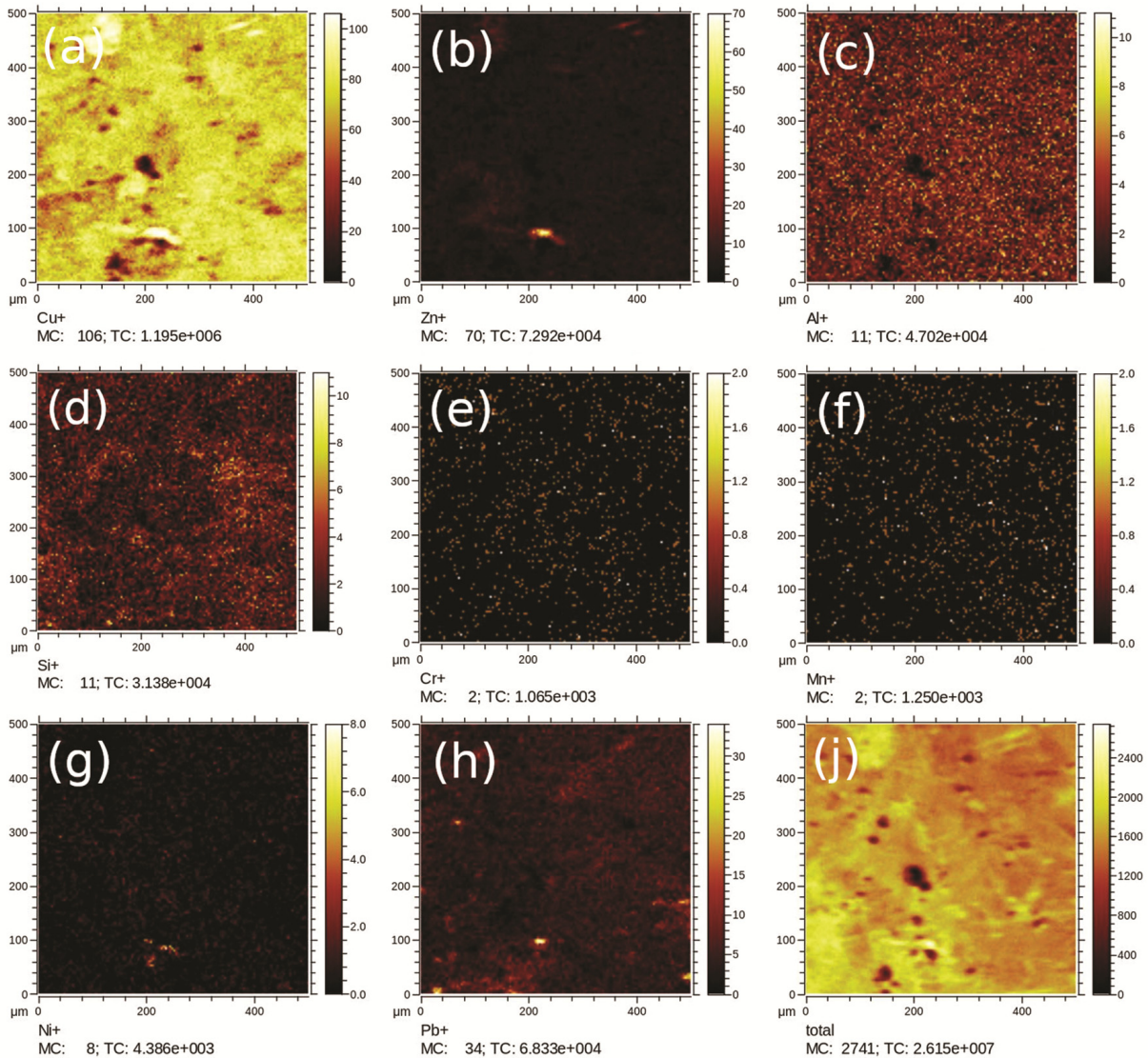
Fig. 3 — Ion image profiles of a representative Scandinavia brass sample, showing positive ion distribution for (a) Cu, (b) Zn, (c) Al, (d) Si, (e) Cr, (f) Mn, (g) Ni, (h) Pb, (i) Zr ions (not shown due to low counts), (j) total ion counts

represent ion counts that are perhaps closer to the true vales for brass of a particular geographical region. In order to match any unknown samples' ions' counts with such normalized statistically averaged data, it may be wiser to compare data from the normalized statistical mean counts from several samples from that region and from several samples, if possible, for a close match. Even in the same geographic region, slight variations of normalized statistical mean ion counts were also observed for samples made over a wide historical time period in some cases. Slight brand to brand variations in normalized statistical mean ion counts from the same geographic region were also observed. However, these are not discussed here in greater detail.

Tables 1-2 suggests that all major and minor constituents from all regions had a lot of variation even though the usage of all brass samples were very similar. So their metal performance properties have to be very similar. Thus the extent of impurity distribution and variation did not significantly affect the materials performance properties of such brass. That is feasible due to variations in their thermal treatments. The normalized statistical mean ion counts of samples from South Asia had less statistical deviation for most of the impurity ions considered (full details omitted for brevity).

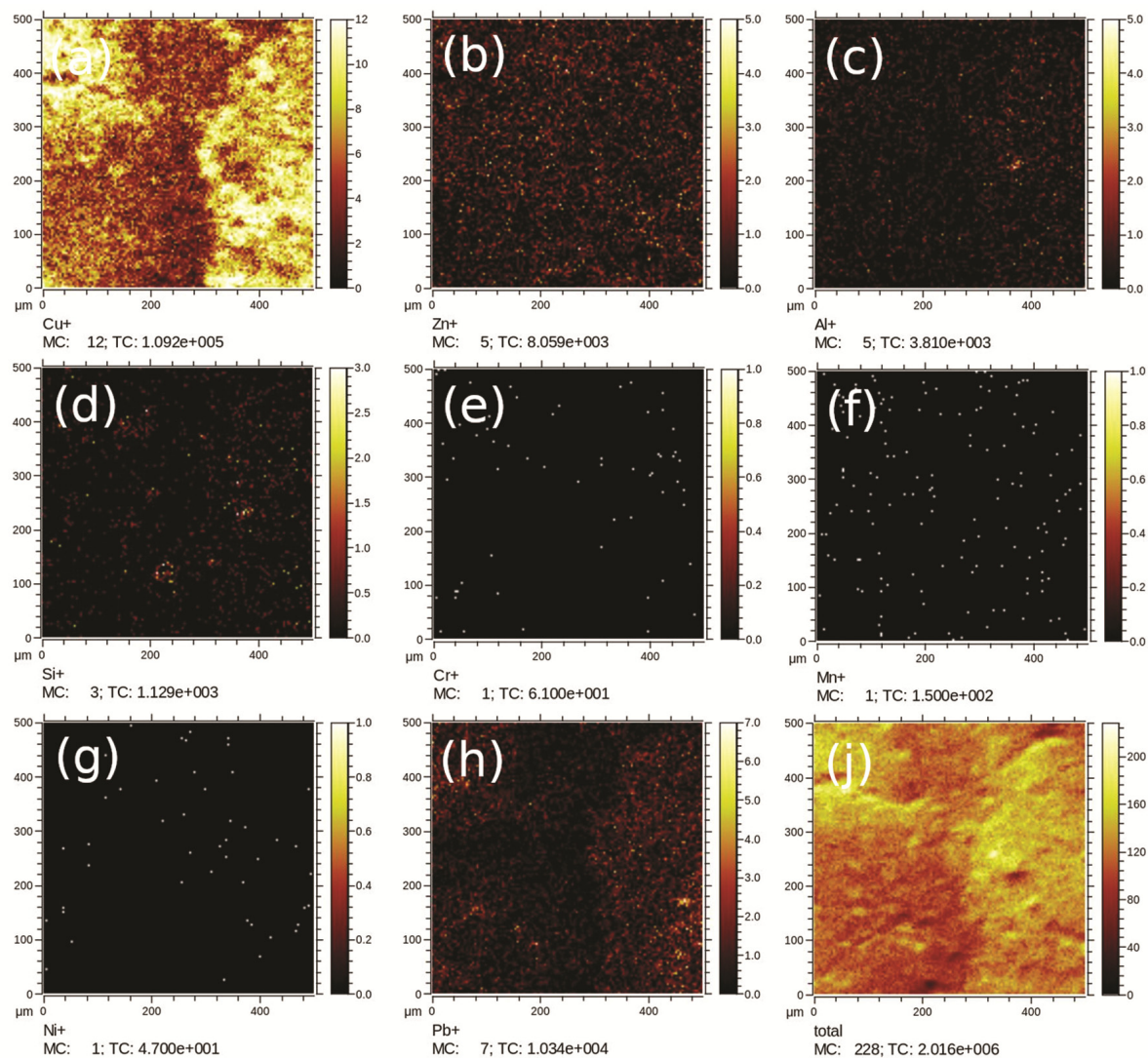We have attempted to co-relate the position of these brass constituents in the periodic table with their

Fig. 4 — Ion image profiles of a representative UK brass sample, showing positive ion distribution for (a) Cu, (b) Zn, (c) Al, (d) Si, (e) Cr (low counts), (f) Mn, (g) Ni (low counts), (h) Pb, (i) Zr ions (not shown due to low counts), (j) total ion counts

performance using their known electron configuration, atomic radii, ionic radii and covalent radii as discussed below.

Copper has an electron configuration of [Ar] $3d^{10}4s^1$ [9,10]. Its atomic radius is 128 pm (picometers), ionic radius is 140pm, and its covalent radius is 132 pm [19]. Zn has an electron configuration of [Ar] $3d^{10} 4s^2$, while its atomic radius is 134pm, ionic radius is 139pm, its covalent radius is 122 pm. Al has an electron configuration of [Ne] $3s^2 3p^1$, while its atomic radius is 143 pm, ionic radius is 184pm, and its covalent radius is 118 pm. Si has an electron configuration of [Ne] $3s^2 3p^2$, while its atomic radius is 111pm, ionic radius is 210 pm, and its covalent radius is 111 pm. Cr has an electron configuration of [Ar] $3d^5 4s^1$, while its atomic

radius is 128 pm, ionic radius is 200 pm, and its covalent radius is 139 pm. Mn has an electron configuration of [Ar] $3d^5 4s^2$, while its atomic radius is 127 pm, ionic radius is 80 pm, and its covalent radius is 139 pm. Ni has an electron configuration of [Ar] $3d^8 4s^2$, while its atomic radius is 124 pm, ionic radius is 83 pm, and its covalent radius is 124 pm. Pb has an electron configuration of [Xe] $4f^{14} 5d^{10} 6s^2 6p^2$, while its atomic radius is 175 pm, ionic radius is 133 pm, and its covalent radius is 146 pm. Zr has an electron configuration of [Kr] $4d^2 5s^2$, while its atomic radius is 160 pm, ionic radius is 86 pm, and its covalent radius is 148 pm respectively.

Since zinc has a smaller covalent radii compared to copper, after alloying it may be easier to make the
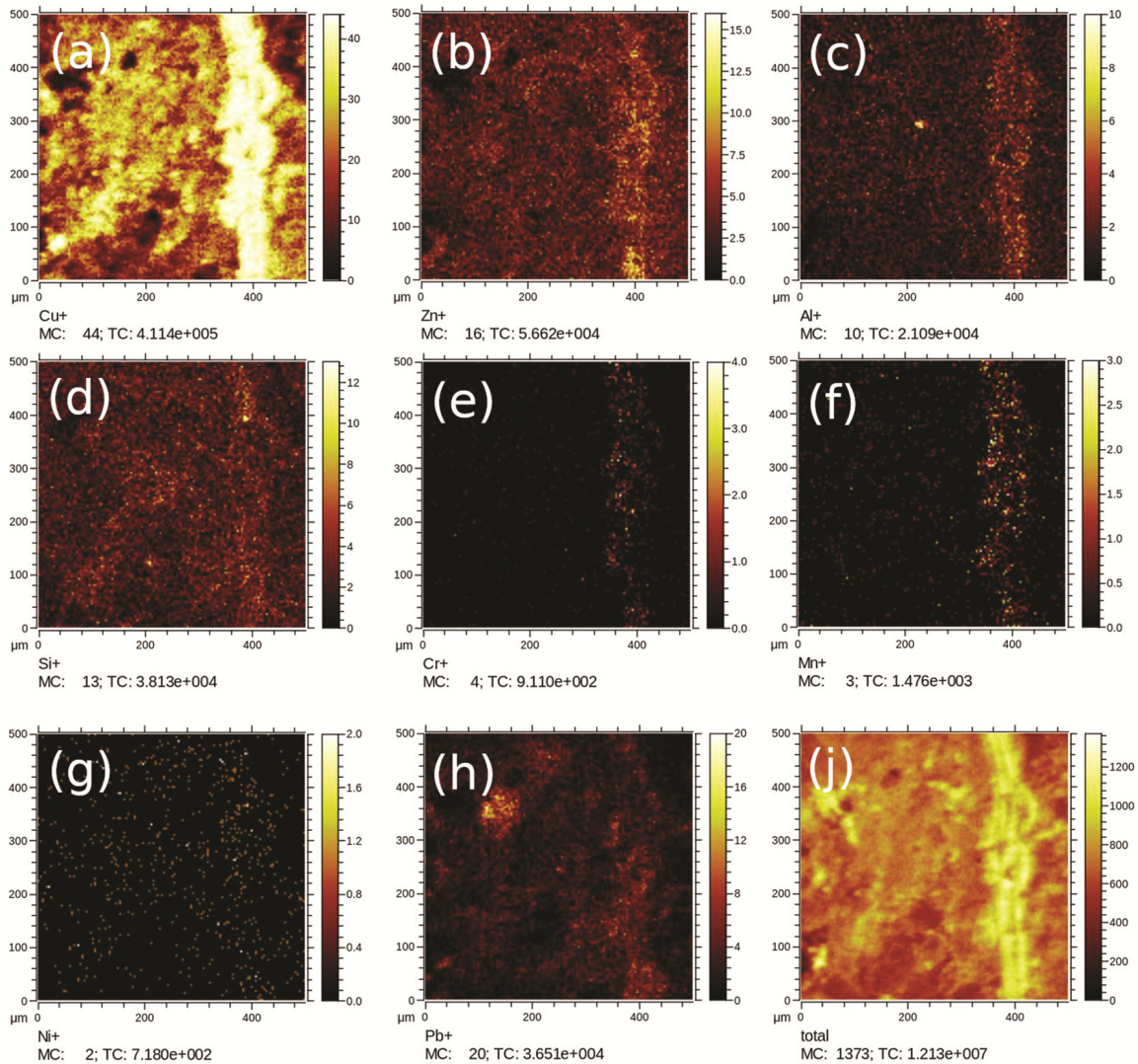
Fig. 5 — Ion image profiles of a representative South Asian brass sample, showing positive ion distribution for (a) Cu, (b) Zn, (c) Al, (d) Si, (e) Cr, (f) Mn, (g) Ni, (h) Pb, (i) Zr ions (not shown due to low counts), (j) total ion counts

alloy more malleable and ductile. So brass is easily machinable. Such machining properties are further improved by using other impurity elements with relatively smaller covalent radii like Al, Si, Ni. In contrast, other impurities with larger covalent radii like Cr, Mn, Pb, will be making the alloy stressed possibly leading to hardening effects. Trace impurities like Zr with negligible normalized ion counts should have no major role in the machining or alloy hardening effects at all.

Pure metal extraction processes used in continental Europe today are automated and requires less human intervention[21]. Such optimized processes leads to extraction of purer metals with less impurities, and relatively less slag. In order to get alloy hardening properties in such pure materials during alloy making, controlled amounts of certain impurities are deliberately used in alloy softening or hardening as the case may be. In contrast, older and more traditional processes used in South Asia need more human inputs and inherently has more impurities and slag by default. So the relative elemental content of Cu and Zn gets reduced. This explains the observed data shown in the Tables 1 and 2. Hence, it may be inferred that unless there is a major change in crystalline property like phase *etc*. along with change in associated micro-crystalline properties like texture etc. with alloying, one cannot expect any drastic change in performance properties of such metal alloys. Experimental data on similar hardness values

Table 1 — Showing Normalized Ion counts using Bi+ ion source for brass from different parts of the world
(calculated statistical mean count value considered)

	Cu	Zn	Al	Si	Cr	Mn	Ni	Pb	Zr
USA	0.0328	0.00462	0.00161	0.00346	6.55E-5	5.95E-5	0.00806	0.00508	4.17E-6
Germany	0.04774	0.00388	0.00141	0.00179	5.17E-5	6.12E-5	1.27E-4	0.00438	3.89E-6
Scandinavia	0.04621	0.00344	0.00141	0.00218	4.65E-5	5.38E-5	1.18E-4	0.00545	3.76E-6
UK	0.0634	0.00753	0.00132	5.35E-4	3.69E-5	5.7E-5	4.4E-5	0.0045	4.48E-6
South Asia	0.0298	0.00214	0.00156	0.00236	2.76E-5	7.82E-5	5.12E-5	0.00478	3.58E-6

Table 2 — Showing Normalized Ion counts using Bi+ ion source for brass from different parts of the world
(statistical median count value considered)

	Cu	Zn	Al	Si	Cr	Mn	Ni	Pb	Zr
USA	0.0284	0.00312	0.00132	0.00353	5.65E-5	3.66E-5	4.17E-5	0.00264	4.31E-6
Germany	0.0451	0.00269	0.00143	0.0014	5.11E-5	6.15E-5	1.24E-4	0.00326	3.79E-6
Scandinavia	0.04502	0.00336	0.00151	0.00146	4.27E-5	4.2E-5	8.38E-5	0.0045	3.58E-6
UK	0.0582	0.00639	0.00119	3.92E-4	2.75E-5	6.76E-5	4.38E-5	0.0011	5.42E-6
South Asia	0.0305	0.00189	0.00162	0.0025	2.21E-5	6.47E-5	2.87E-5	0.00464	3.33E-6

of these different brass samples from different parts of the world would have been able to prove this point on the ability of differences in thermal treatments to compensate for slight differences in composition. All these brass samples have minute stamping marks of their manufacturer on the flat surface. Their other surfaces are curved, making them practically unsuitable for micro-hardness measurements. However, deducing such logic may be improper based on only one metal alloy system as used here. Hence, other different aluminum alloys and their properties as reported in literature were considered for discussion to understand the effect of alloy composition on such performance properties like hardness.

There are no known comparable studies in literature of other metal alloys using TOF-SIMS which may be used to show variation in composition and its correlation with change in crystalline properties either.

In Al-Si-Cu aluminum alloys, the micro-hardness measurement data had showed a small 10% variation with change in the constituents[21]. The same logic about covalent radii numbers may be used here as well. In case of Al-Sc-Zr alloy systems, after variation of all possible parameters, the micro-hardness values could be changed by 3 times[17] while others report negligible changes[18]. In Al-Si systems, with alloying, the micro-hardness values could be changed by 40% or so[19], while others report a change of only up to 20% in micro-hardness values[20]. In 5083-AlC alloys, the alloying variation could change the micro-hardness by a factor of 2[21]. In 6061-Al alloy and 2024-Al alloy, the micro-hardness changed with alloying content by about 50% or so[22]. Drastically changed hardness values were

thus seen only when there was a crystalline phase transition during alloying. Based on all such reported observations on aluminum alloys, including Al-Cu systems[23], it was deduced that unless there is a major change in crystalline property like phase *etc*. along with change in associated micro-crystalline properties like texture, hardness *etc*., due to alloying, perhaps one does not observe any drastic change in metal alloys' performance. Thermal treatments may be able to moderate or compensate for some of the variations in composition by varying the differences in micro-crystalline parameters of these alloys, unless there is phase change. This is perhaps applicable in general for most alloying systems. It is felt that the present methodology using TOF-SIMS technique may also be extended to analysis of other metals, metal alloys, polymeric blends and possibly even tissue to know how composition variation can vary the properties.

4 Conclusions

A methodology was developed to normalize TOF-SIMS ion counts of metal alloys like brass based on its ion mass and image based data. Under appropriate ultra-high vacuum conditions, by comparing normalized ion counts, *ie*. ion counts for each ion divided by total ion counts in the mass spectra of two alloys under comparison, two sets of ion counts' of mass spectra of two groups of different but similar samples collected from two similar instruments using similar experimental conditions can be compared using their statistical mean values. Such data are obtained from the ion image data captions. Due to such a normalization process, TOF-SIMS data collected on different dates on similar alloy samples

can be normalized and compared using their statistical mean counts. Here brass and its constituents have been used for analysis – but this methodology is extendable to other metals, alloy materials or polymers as well if analyzed in a similar manner using TOF-SIMS. Thus, inter-comparison of similar materials' using TOF-SIMS mass spectral data is possible using similar ion beams and similar UHV conditions. The end use of the compared brass samples for different zones were the same, with similar performance requirements. They are also subjected to appropriate non-identical thermal and physical treatments required to get these desired proprieties, in spite of a difference in their constituents' relative normalized statistical mean ion counts. Based on published variation in properties of aluminum alloy systems with composition and their studies, it was felt that unless there is a drastic change in crystalline phase or micro-crystalline properties, alloying in general, may not drastically change material properties.

Acknowledgments

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