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Application of particle-induced X-ray emission, backscattering spectrometry and scanning electron microscopy in the evaluation of orthodontic materials

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Abstract The focus of this investigation was on orthodontic materials used in the manufacture of dental brackets. The properties of these dental materials are subjected to various physical parameters such as elongation, yield strength and elasticity that justify their application. In turn, these parameters depend on the quantitative elemental concentration distribution (QECD) in the materials used in the manufacture. For compositional analysis, proton-induced X-ray emission (PIXE), backscatter spectrometry (BS) and scanning electron microscopy (SEM) were applied. QECD analysis was performed to correlate the physical parameters with the composition and to quantify imperfections in the materials. PIXE and BS analyses were performed simultaneously with a 3 MeV proton beam while electrons accelerated at 25 keV were used for the SEM analysis. From the QECDs it was observed that: (1) the major elements Cr, Fe and Ni were homogeneously distributed in the orthodontic plate; (2) the distribution of Mo and O correlated with one another; (3) there was a spread of Cr around regions of high C concentration; and, (4) areas of high concentrations of Mo and O corresponded to a decrease in C concentrations. Elemental concentration correlations are shown to indicate the similarities and differences in the ease of formation of phases, based on the tangent of linearity.

Keywords Particle-induced X-ray emission
Backscattering Scanning electron microscopy
Orthodontic material Quantitative elemental concentration distribution

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Introduction

For the past two decades, advances in metallurgy and the biocompatibility of dental alloys has been the target of extensive research in orthodontics, with the emphasis on mechano-therapy [1]. Studies in this area have generated many unanswered questions, confirming the need for further research into the biocompatibility and hypersensitivity responses of materials used in the manufacture of orthodontic appliances. Materials used in dental applications must have specific characteristics such as biological safety and functionality, adequate tissue response and resistance to corrosion. As such, metal alloys have been extensively used because of their elasticity, hardness and stress resistance. While the biocompatibility of orthodontic alloys is widely reported, what is not well known is the level at which a patient is exposed to toxic doses of metals from orthodontic appliances [2]. Given that this process is not thoroughly understood, orthodontists are hard pressed to select a suitable and biologically safe alloy for their patients [3]. The bio-compatibility and mechano-therapeutic application of these alloys are directly correlated to its elemental composition. However, the elemental composition indicate only the presence of elements in the orthodontic material and not the concentration distribution of these elements within the material [4]. Investigation of key physical and mechanical properties of materials used for the manufacture of dental brackets may provide a basis for its intra-oral performance and may assist the clinician in selecting optimum handling and application in mechano-therapeutical configurations. The aim of the study was to explore the use of

complementing nuclear analytical techniques to determine the composition and distribution of elements in orthodontic materials used in the fabrication of dental brackets.

Stainless steel alloys are widely used in the manufacture of orthodontic materials. Various metals are incorporated in the matrices of alloys serving different purposes. Carbon and nitrogen are introduced in a steel alloy as hardening agents. Carbon, in particular, strengthens iron by distorting its crystal lattice. Nitrogen is effective in improving the mechanical and anti-corrosion properties of steels, where it precipitates as very fine and coherent nitrides. When nitrogen is added to austenitic steels it can simultaneously improve fatigue life, strength, work hardening rate, wear and localized corrosion resistance. Blowing oxygen through molten pig iron lowers the carbon content of the alloy and changes it into low-carbon steel.

Chromium added to a steel matrix makes it resist rust, or more stain 'less' than other types of steel. When chromium is present in the steel, it combines with oxygen in the atmosphere to form a thin, invisible layer of chrome-containing oxide, referred to as the passive film. Because of the large atomic radius, the sizes of chromium atoms and their oxides are similar, hence they pack neatly together on the surface of the metal, forming a stable layer only a few atoms thick. If the alloy is cut or scratched and the passive film is disrupted, more oxide will speedily form and recoat the exposed surface, protecting it from oxidative corrosion. Nickel alloys are used extensively because of their corrosion resistance, high temperature strength and their special magnetic and thermal expansion properties. When added to steel, molybdenum enhances strength, hardenability, weldability, toughness, elevated temperature strength and corrosion resistance. In a nickel-based alloy, such as in dental alloys, it improves both corrosion and high-temperature creep deformation.

Non-alloying elements, referred to as residual elements, are those that have not been intentionally incorporated into the matrix, but are present in the ore. These elements are normally in the ppm concentration range. Of these, copper in steel alloys tie up highly oxidative elements such as tin, should it be present. Zinc as a residual element has a low electrochemical potential and hence decreases the oxidation of most elements, acting as a sacrificial element. Moreover, zinc provides less marginal breakdown and so increases the clinical performance of the alloy.

Experimental

Orthodontic alloy materials were obtained in the form of rods, plates and wires. The Nuclear Microprobe (NMP) facility at the Materials Research Department at iThemba LABS, Faure, South Africa was used for the irradiation of the materials [5]. A 3 MeV beam of protons was obtained from a high voltage engineering 6 MV Van de Graaff accelerator. Specimens were cleaned with copious amounts of Millipore water and left in a close environment to dry. Since the samples were all in metallic form, it was not necessary for carbon coating. Irradiation was maintained to 1 9 10^6 counts as a minimum. Micro-PIXE data were obtained with a high purity germanium (HPGe) detector (Princeton Gamma Tech) with a resolution of 154 eV at Mn K_a at 5.90 keV and was positioned at an angle of 135 to the incoming proton beam. An absorber of 102 lm thick Al was used for X-ray attenuation. Where necessary, a thicker absorber (150 lm Al) was used to attenuate the emission of the higher z elements. Micro-BS data were obtained with a surface barrier detector, positioned at 176 to the incoming beam. Because of the versatility of the specially designed scattering chamber of the nuclear microprobe facility at iThemba LABS, the PIXE and BS analysis was performed simultaneously [5]. The areas scanned were in dimensions of a minimum of 200 lm 9 200 lm for PIXE, BS and SEM. To ensure that the area to be analysed by PIXE and SEM was the same, a small region of area 1.8 lm 9 1.8 lm (the size of the proton beam) was over-exposed during the PIXE analysis, as a demarcation. SEM analysis was performed after the PIXE and BS analysis.

To ascertain any correlations in the elemental concentration distributions, elemental maps were constructed off-line using the Dynamic Analysis methodology, contained in the GeoPIXE computational software [6, 7]. Elemental distribution correlations were also obtained. The software programs SimNRA [8] and RUMP [9] were used for quantification of the backscattered data. SEM analysis was performed with a Jeol Scanning Electron Microscope to evaluate the chemical composition of the brackets. The working distance was 4 mm, the tilt angle 0.0 and 39.43 for the take-off. The electron accelerating energy was 25 keV and the amplitude was 50 Hz. The detector used was a SUTW, Sapphire with a resolution of 145 keV. The live-time duration was 300 s to improve the level of confidence in the data accumulation. A peak to background ratio of greater than 0.09 and an integration error of less than 2 % were considered statistically significant. The background determinations for PIXE and SEM are different due to manufactures' preferences. More so, the present background determination of the SEM manufacture EDAX software yielded under-estimated values. For this reason and for comparative analysis, background determination of the X-ray emission data was based on the equation.

$$y = \frac{a}{2d}\exp\left(\frac{b}{d} + \frac{E}{2d^2} + \frac{c^2}{d}\right) - \operatorname{erf}\left(\frac{b}{\sqrt{2}d} + \frac{E}{\sqrt{2}c}\right) + d \quad (1)$$

The equation is an exponential modification of the normal Gaussian relationship (Mars and Gihwala, unpublished data). y is the counts, E is the energy in keV and *erf* is the error function. The constants are *a, b, c* and *d* which are determined by the fit to the data, with $c \neq 0$ and $b = 0$ as constraints. a is the minimum energy at which data were accumulated. b is the energy at which maximum background radiation occurred. c and d respectively account for the energy at which the analysis was performed and for the lower background radiation as the analysis energy is approached, that is near 25 keV. A minimum of 4.5×10^5 counts were accumulated for each analysis. The data were quantified with the manufacturer's EDAX software program, which included the Z, A and F corrections.

The elastic modulus was obtained with an Intestron instrument. The conversion of bulk (K) modulus to elastic (E_m) modulus was made using the equation $K = \frac{E_m}{3(1-2r)}$ where r is the Poisson ratio (0.271 for this study).

Results and discussions

The scanning electron micrograph of the orthodontic plate is shown in Fig. 1, the marked differences in intensities of the dark and light areas are observable. These intensities correspond to different elemental concentration distribution. The percentage compositions of the dark and light areas are given in Table 1.

Most marked in the differences are carbon, which has a higher concentration in the dark area than in the light area; oxygen which has a lower concentration in the dark area than in the light areas; both zinc and sulphur which have higher concentrations in the darker region can be attributed to ZnS (zintl) phases dispersed throughout the matrix.

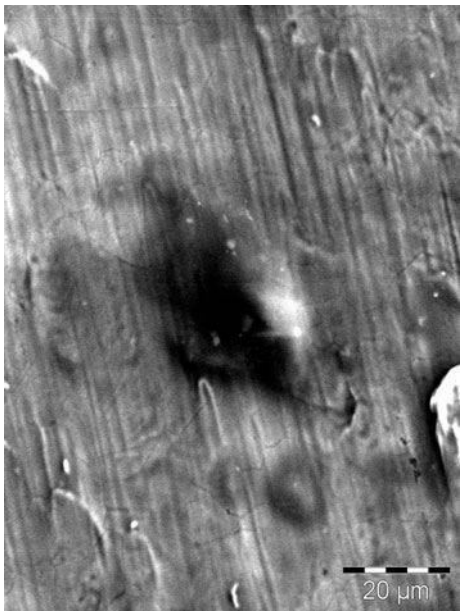


Fig. 1 Scanning electron micrograph (80 × 100 μm) of the orthodontic plate, illustrating the *light* and *dark* areas. The *scale bar* is 20 μm

An increase in carbon concentration relates to a corresponding decrease in both iron and chromium concentrations and to some extent, a decrease in copper concentration. The decrease is the highest for chromium, followed by iron and then copper. On the other hand, for the increase in oxygen concentration there is a corresponding increase in both iron and copper concentrations.

The aluminium and nickel concentrations remain the same throughout the scanned area. Hence, the elemental distributions of these elements are not affected by the distribution of other elements in the matrix.The graphical representation of the micro-PIXE data as a spectrum is shown in Fig. 2. For all the elements, the K_a X-ray intensities were used.The Si escape peaks are shown to indicate the overlapping with the Ti and V X-ray lines. The graphical representation as a spectrum of the micro-SEM data is shown in Fig. 3. The corresponding similarity for the energy region 4–10 keV for both spectra is observable.

The micro-PIXE quantitative elemental concentration distributions of the elements chromium, manganese, iron, copper, zinc and molybdenum are given in Fig. 4. All these elements, except zinc are homogenously distributed throughout the matrix of the orthodontic plate.

Zinc is inhomogeneously distributed and since it acts as a reductant, it can significantly affect the clinical performance of the orthodontic plate. The micro-BS quantitative elemental concentration distribution of the O and C is given in Fig. 5. Of these, the carbon concentration distribution is inhomogeneous. Correlations of element concentrations were determined based on the area of the alloy analysed. These correlations were used to detail the dependency of the formation of binary element phases, which is directly related to the tangent of linearity a two-element correlation. The tangent of linearity is defined as the measure of the angle the line of linearity makes with the horizontal axis. Hence, if the line of linearity is parallel or coincides with the horizontal axis then the distribution of the element represented on the horizontal is independent of the distribution of the element represented on the vertical axis (Fig. 6).

While the correlations of iron with both carbon and oxygen are more diffused that the correlations of chromium with carbon and oxygen, these correlations are all predominantly linear. With respect to oxygen, the tangent of linearity for chromium and iron is virtually the same which indicates that the ease of formation of phases of oxygen with chromium and iron is the same. However, the iron correlation with oxygen is predominantly in the oxygen

Table 1 The weight percentage (wt%) composition, based on electron- and proton-induced X-ray emission data, of elements in the dark and light areas as observed in the scanning electron micrograph of the orthodontic plate

Elem	Dark area			Light area			Manufacturer's
	SEM	PIXE	BS	SEM	PIXE	BS	Specifications
C	5.0 ± 0.5	ND	4.8 ± 0.8	2.6 ± 0.7	ND	2.5 ± 0.8	4.6 ± 0.8
O	1.5 ± 0.3	ND	1.5 ± 0.8	2.2 ± 0.6	ND	2.4 ± 0.8	1.6 ± 0.4
Al	0.3 ± 0.2	ND	ND	0.3 ± 0.2	ND	ND	0.2 ± 0.1
Si	1.2 ± 0.31	ND	ND	1.0 ± 0.3	ND	ND	1.1 ± 0.2
S	0.4 ± 0.2	ND	ND	0.2 ± 0.1	ND	ND	NS
Ti	0.7 ± 0.2	0.84 ± 0.18	ND	0.8 ± 0.3	0.76 ± 0.09	ND	1.1 ± 0.4
V	0.4 ± 0.2	0.31 ± 0.09	ND	0.3 ± 0.2	0.33 ± 0.06	ND	NS
Cr	15.7 ± 0.5	17.45 ± 0.42	ND	16.4 ± 0.5	17.01 ± 0.08	ND	17.5 ± 0.3
Mn	1.0 ± 0.3	1.15 ± 0.08	ND	1.0 ± 0.3	1.19 ± 0.07	ND	1.1 ± 0.2
Fe	59.0 ± 0.5	67.58 ± 0.28	ND	67.0 ± 0.5	62.85 ± 0.14	ND	64.5 ± 0.8
Ni	8.7 ± 0.8	8.95 ± 0.15	ND	8.7 ± 0.5	8.55 ± 0.06	ND	8.7 ± 0.4
Cu	ND	80 ± 10 ppm	ND	ND	60 ± 10 ppm	ND	NS
Zn	ND	130 ± 12 ppm	ND	1.1 ± 0.5	120 ± 10 ppm	ND	NS
Mo	ND	120 ± 10 ppm	ND	ND	110 ± 10 ppm	ND	NS

Back scattering data are also provided

Where applicable, some concentrations are presented in ppm. All peak-to-background ratios were greater than 0.1 and the peak integration errors were less than 5 %. *ND* the element concentration could not be determined with the analytical technique, *NS* not specified

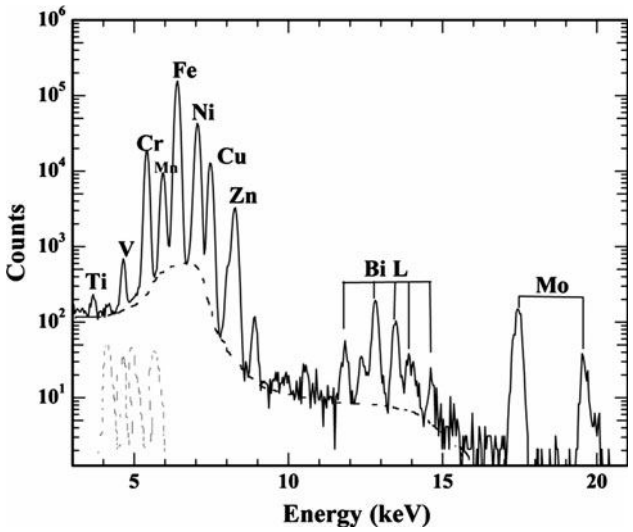


Fig. 2 The spectrum as a graphical representation of the micro-PIXE data of the orthodontic plate, obtained with a 3 MeV proton beam. The *solid line* represents the data and the *broken line* the GeoPIXE fit to the data. The *dotted line* represents the Si escape peaks

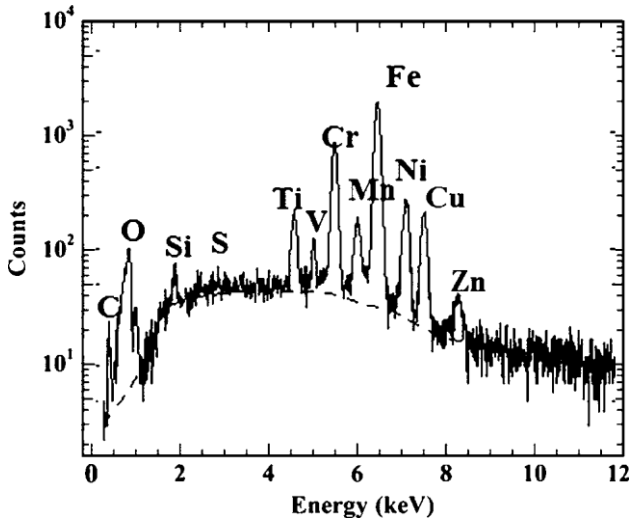
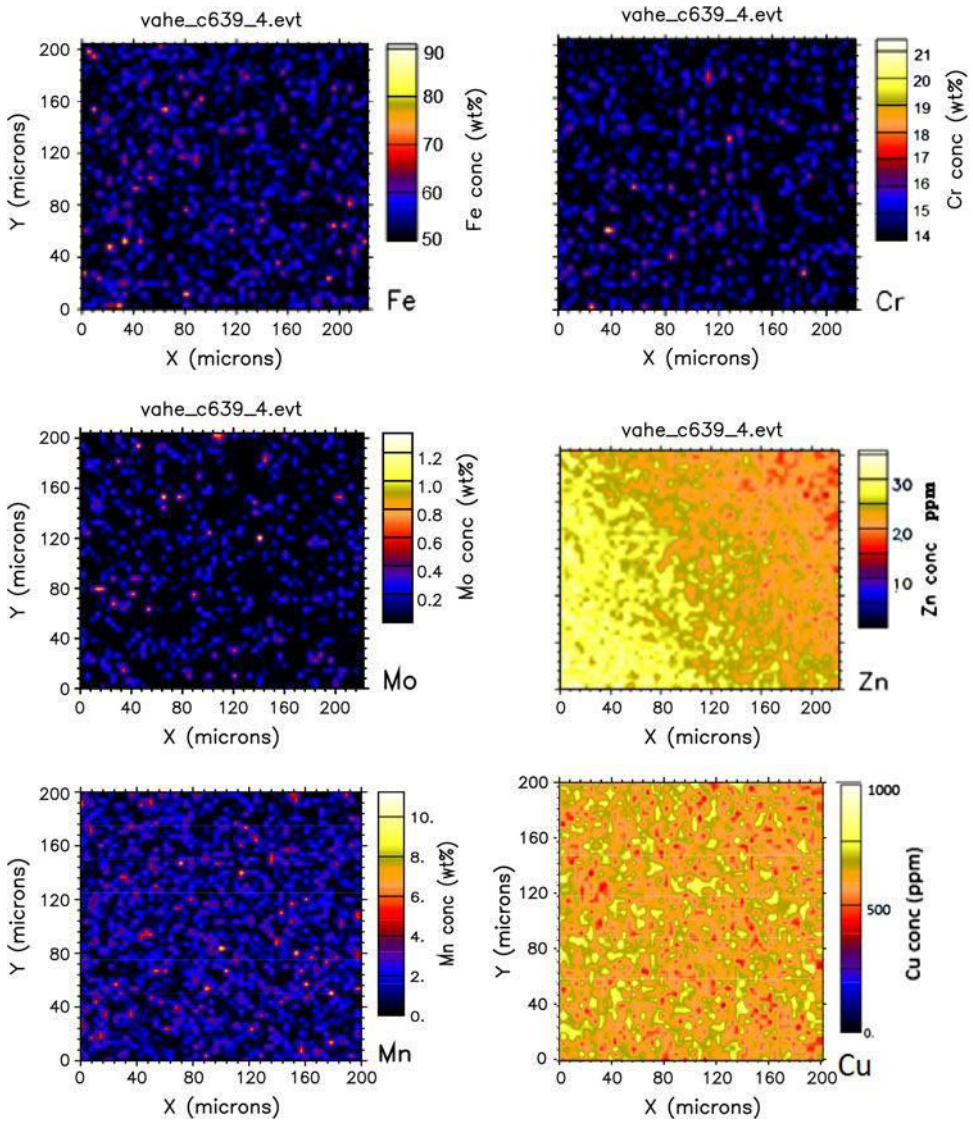


Fig. 3 The spectrum as a graphical representation of the micro-SEM data of the orthodontic plate, obtained with a 25 keV electron beam. The *black line* represents the data, the *dotted line* the fit to the data. The *broken line* is the minimal background fit (using Eq. 1) to the data

concentration range of 3.5–5.0 wt%. The corresponding iron wt% ranges from 62 to 65 wt%.

For chromium, the tangent of linearity of the correlation with carbon is less than the tangent of linearity of iron with carbon. This indicates that the ease of formation of Fe–C phases is kinetically more feasible the ease of formation of the Cr–C phases. Hence, the matrix contains mostly the Fe–C phases.

The manufacturer's specification for the bulk modulus for the raw alloy is given as 162.7 GPa. The value obtained in this study for the orthodontic bracket is 155.5 GPa which indicates that there was a marginal decrease in resistance to



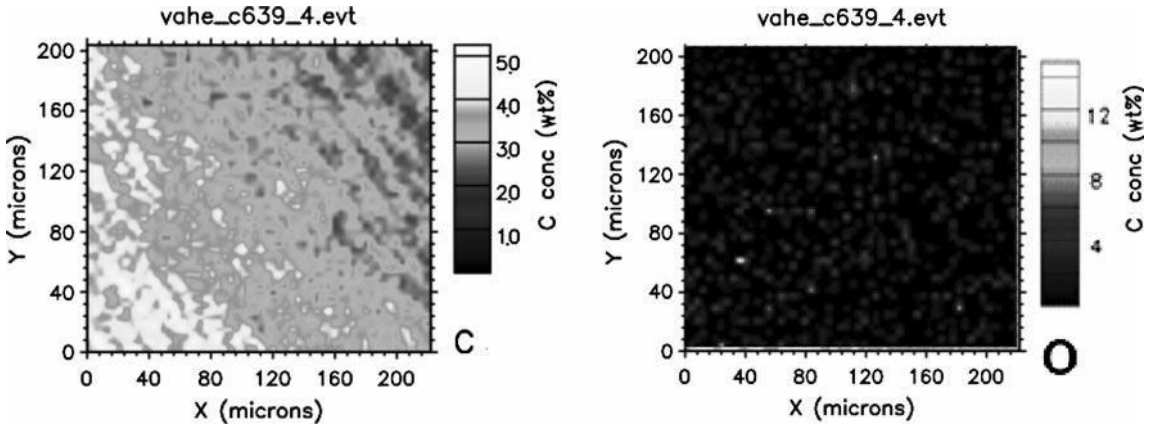


Fig. 4 The micro-PIXE quantitative elemental concentration distributions of the elements FE, Cr, Mo, Zn, Mn and Cu. The dimensions of the area scanned was 200 lm 9 200 lm

Fig. 5 The micro-BS quantitative elemental concentration distributions of the elements C and O. The area scanned was 200 lm 9 200 lm

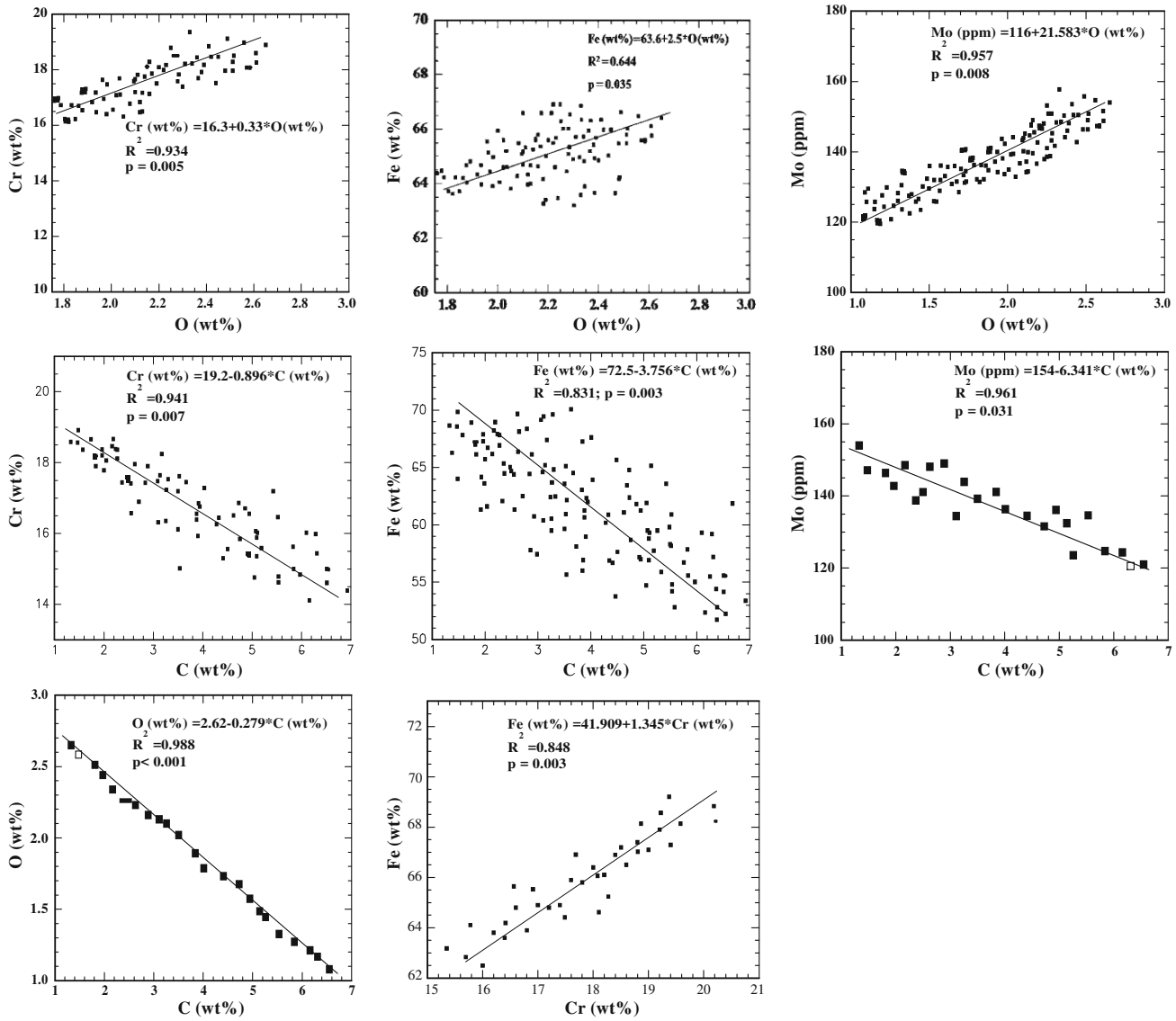


Fig. 6 Graphs of composition correlations of Cr, Fe and Mo with O, Cr, Fe and Mo with C, O with C and Fe with Cr. The difference in linearity of the correlations is observable. The correlations of Fe with C and O are more diffused than the correlations of Cr with C and O. Areas of high concentrations of Mo and O corresponded to a decrease in C concentrations

uniform compression of the alloy after the artefact was produced.

Conclusions

The use of the analytical techniques of SEM, BS and PIXE proved that the quantitative elemental concentration distributions in the orthodontic plate could be ascertained. The use of SEM and the complementarity of BS showed that there is oxygen present in the matrix and that the oxygen presence could be correlated to the distribution of various other components such as iron and molybdenum present in the matrix. The presence of oxygen also determines the degree of corrosivity of the materials. The presence of carbon in the matrix and its inhomogeneity and correlation to other components could also be verified. Because of its presence and its inhomogeneous distribution, the elasticity physical parameter of the plate will be decreased. This was proven by the value determined for the bulk modulus.

It is recommended that the degree of inhomogeneity of the elemental distribution be quantified and then used to theoretically determine the effects of the inhomogeneity on the physical parameters of the dental materials.