EVALUATION OF THE MAGNETIC PROPERTIES OF Ag-Au-Pd-Cu DENTAL ALLOYS

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The paper discusses four Ag-Au-Pd-Cu dental alloys, with different chemical compositions, which are used to produce fixed dental-prosthetic structures. These dental alloys must have a low level of biological risk after being implanted in the oral cavity, which means minimal release of ions from their surface, or the absence of corrosion, and, recently, the absence of ferromagnetism has been introduced as an additional requirement. The latter requirement is particularly important when magnetic resonance (MR) is used in the medical diagnosis of a patient who has an implanted fixed dental-prosthetic structure. With this technique, the internal structure of the human body is imaged using a strong magnetic field, radio waves and computer technology. Therefore, the absence of ferromagnetic, embedded biomaterials is necessary in the part of the body where medical diagnostics are performed. Microstructural investigations of four Ag-Au-Pd-Cu dental alloys (Auropal S, Auropal SE, Midor S and Midor SE) and measurements of their magnetic properties were carried out as part of the research. The results showed that Ag-Au-Pd-Cu dental alloys have a stable microstructure, which allows them to be processed later into fixed prosthetic constructions. The measurements of the magnetic properties showed that the Ag-Au-Pd-Cu dental alloys are diamagnetic.

Keywords: magnetic properties, noble dental alloys, characterisation

1 INTRODUCTION

The strategy of developing dental materials is related to the development of biomedical and biotechnical sciences in the restorative disciplines.1–3 These are closely related to various types of dental materials, among which dental alloys occupy a special place. The European Union Medical Devices Directive 93/42 EEC harmonised the laws regarding medical devices on the European Union market, to achieve a high level of quality of these products for patient safety. Products for the European market that comply with the Medical Devices Directive must bear the CE mark. In 2017, a new regulation for medical devices was issued, (EU) 2017/745, which brings innovations regarding the requirements for these products. The transition period for the implementation of the requirements of the new MDR (Medical Device Regulation) was 3 years, and ended on May 26, 2020.

Knowledge of the physico-mechanical properties, biological acceptability and functional properties of dental alloys is crucial for dental use.4,5 Functional properties are highlighted here; they are not classified on the basis of their origin, nature of bonding or processing techniques, but on the functions that they can perform. In the Periodic Table only some elements have magnetic properties. These elements are iron, nickel and cobalt. In nature and in our immediate environment, these elements are most often found in mixtures or alloys. Magnetic properties are related to magnetism, which is a physical phenomenon where certain substances exert a repulsive or attractive force on other substances. This causes the movement of charged particles, which causes
the formation of a magnetic field (Figure 1). Magnetism is present in all substances, but in some substances it is so weak that we cannot detect it without special preparations. The resulting magnetic field is a vector field around permanent magnets or conductors, through which an electric current flows. In this field we perceive the magnetic force. It is illustrated by lines of force – lines that originate from the north pole of a magnet and converge to its south pole. The tangent to the line at each point is the magnetic field density.

Several types of magnetism are known. Diamagnetism results from the movement of electrons in atoms. It is a phenomenon that occurs when the density of the magnetic field in a substance placed in a magnetic field is slightly lower than the density of the magnetic field outside this substance (this means that the substance pushes the magnetic field out of itself). It is present in all substances, except for paramagnetic and ferromagnetic substances, where other, stronger phenomena dominate. Perfect diamagnets include superconductors that push out the magnetic field completely. Paramagnetism is a phenomenon when the density of the magnetic field in a substance placed in a magnetic field is slightly greater than the density of the magnetic field outside this substance (it is considered that the relative permeability $\mu_r > 1$). Such substances are called paramagnetic, and usually $\mu_r$ is only slightly greater than 1. The paramagnetism originates from the electron’s own magnetic moment, which is not a consequence of its motion. In an external magnetic field, the magnetic moments in a paramagnetic substance behave like magnetic fields, and are partially arranged so that, on average, a few more of them point in the direction of the external magnetic field. Ferromagnetism is the phenomenon whereby the density of the magnetic field in a substance placed in a magnetic field is much greater than the density of the magnetic field outside that substance. Ferromagnetism is the result of the fact that magnetic dipoles in ferromagnetic substances within macroscopic regions arrange themselves spontaneously and are arranged even outside the magnetic field. In an external magnetic field, the magnetic moments of these domains are in the direction of the external magnetic field. Unlike paramagnetism, which is present in both solids, liquids and gases, ferromagnetism is only present in rare solids. Among them are iron, cobalt, nickel and some alloys.

The magnetic properties for all types of dental alloys in the form of fixed dental structures embedded in the human body are important in medical diagnostics. One of the non-invasive medical diagnostic methods is magnetic resonance (MR), in which the internal structure of the human body is imaged with the help of a magnetic field, radio waves and computer technology. The imaging shows in detail the structures inside the skull, spine, limbs, and especially the soft tissues of the head and body. The results make it possible to detect and locate any injuries, neoplasms, or other abnormalities, and thus help to diagnose the patient’s health problems, and, consequently, to the success of the treatment. In the general instructions for the preparation and course of the MR examination, it is written that, before entering the examination room, it is necessary to remove all metal objects from the body that are magnetic. Metals susceptible to magnetic fields may cause movement or heating during the examination, which can lead to a potential health and safety risk for patients. This is especially true when examining the head or neck, where patients may also have dental prostheses fitted. The problem arises when the dental prosthesis is fixed and cannot be removed. A key role in this form of research is played by the phenomenon of ferromagnetism, when the magnetic field density in a substance placed in a magnetic field is much higher than the magnetic field density outside this substance. This phenomenon is characteristic of Fe, Co, Ni and some alloys, while the phenomenon of ferromagnetism should be completely absent in precious metals and alloys. However, it was shown that some ferromagnetic impurities, present even in a precious metal alloy, may cause MR examination artefacts, which may be misleading for the medical diagnosis.

The dental alloys produced by Zlatarna Celje d.o.o. are noble, and in this study the following Ag-Au-Pd-Cu based alloys were used for research: Auropal S, Auropal SE, Midor S and Midor SE. Their microstructure and magnetic properties were investigated with appropriate research equipment. The aim was to investigate whether these dental alloys have the property of being non-ferromagnetic, and thus not posing a risk in MR examinations. This would mean that the investigated dental alloys of Zlatarna Celje do not prevent the performance of MR examinations, even if the patient has them embedded in the oral cavity.
2 EXPERIMENTAL PART

2.1 Preparation of dental alloys

Metals with a purity of 99.99 % were used for the preparation of the Ag-Au-Pd-Cu dental alloys. The chemical compositions of the prepared Ag-Au-Pd-Cu dental alloys are given in Table 1. The Ag-Au-Pd-Cu dental alloys were melted in crucibles made of pure Al₂O₃ with Ar 5.0 blowing, so that casting took place at a temperature of 1150 °C. The ingots were cast with a diameter of \( \Phi = 10 \text{ mm} \).

<table>
<thead>
<tr>
<th>Ag-Au-Pd-Cu dental Alloy</th>
<th>Au</th>
<th>Pd</th>
<th>Ag</th>
<th>Cu</th>
<th>Zn</th>
<th>Ir</th>
<th>In</th>
</tr>
</thead>
<tbody>
<tr>
<td>Midor S</td>
<td>46.0</td>
<td>6.0</td>
<td>39.5</td>
<td>7.5</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>/</td>
</tr>
<tr>
<td>Midor SE</td>
<td>40.0</td>
<td>4.0</td>
<td>47.0</td>
<td>7.5</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Auropal S</td>
<td>10.5</td>
<td>21.0</td>
<td>58.2</td>
<td>9.3</td>
<td>&lt;1</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Auropal SE</td>
<td>2.0</td>
<td>25.0</td>
<td>64.0</td>
<td>8.0</td>
<td>&lt;1</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

The Ag-Au-Pd-Cu ingot casting was followed by a thermo-mechanical treatment process from profile rolling, annealing and strip rolling, whereby the process is fully protected by national patents. Figure 2 shows the final Ag-Au-Pd-Cu dental alloy plates, ready to be used by dental laboratory technicians for the further casting of dental restorations.

2.2 Microstructural characterisation of Ag-Au-Pt-Cu dental alloys

The specimens for metallographic examination were prepared according to the usual procedure: cold investment in a polymer mass, brushing with sandpapers from grit 80# to 4000#, polishing with diamond paste with granulation between 6 μm and 1 μm.

The microstructure was examined on a Nikon Epiphot 300 Inverted Metallurgical Microscope (Nikon Corporation, Tokyo, Japan), while the chemical analysis was performed with an X-ray fluorescence (XRF) analysis instrument NITON XL3t GOLDD+ (Thermo Scientific NITON Analyzers LLC, Billerica, Massachusetts, USA). XRF uses the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by being bombarded with high-energy X-rays. The phenomenon is used widely for elemental analysis and chemical analysis, particularly in the inves-
tigation of metals, glass, ceramics and building materials, and for research in geochemistry, forensic science, archaeology and art objects.

2.3 Measurements of ferromagnetism

The measurements were carried out on a SQUID magnetometer at the Institute of Physics, Belgrade, Serbia. The Quantum Design MPMS 5XL SQUID Magnetometer with the Evercool system uses a SQUID (superconducting quantum interference device) detector to measure very small changes in magnetic flux, and is extremely sensitive in all AC and DC magnetic measurements. Magnetic moments up to 10^8 emu (10^{-11} Am^2) can be measured reproducibly. MPMS works in the temperature range from 1.9 K to 400 K, and the superconducting magnet can achieve magnetic fields between -5 T and 5 T. The Ag-Au-Pd-Cu dental alloy plates had dimensions of 2 mm x 2 mm with a thickness of 1 mm, and were polished and cleaned in an ultrasonic cleaner before the measurement of ferromagnetism. The measurements on the Ag-Au-Pd-Cu dental alloys were performed in the magnetic field range between -1 T and +1 T.

3 RESULTS AND DISCUSSION

3.1 Microstructure and chemical composition

The binary Au–Ag, Au–Pd and Ag–Pd alloys of Ag-Au-Pd dental alloys (Auropal S, Auropal SE, Midor S and Midor SE) form a continuous series of solid solutions over a wide range of compositions and temperatures (Figure 3). The ternary Ag-Au-Pd alloys are, thus, likely to form single-phase solid solutions. Additionally, the fourth component in these alloys, Cu, is able to form solid solutions with Au and Pd across all compositions, while it is soluble in Ag up to 14.1 at.% Cu, in the range of solubility for the examined dental alloys. The resulting solidification temperature range of the alloys was narrow – as shown in Table 2.

Table 2: Melting intervals of the Ag-Au-Pd-Cu dental alloys

<table>
<thead>
<tr>
<th>Ag-Au-Pd-Cu dental Alloy</th>
<th>Melting interval (in °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Midor S</td>
<td>850 – 920</td>
</tr>
<tr>
<td>Midor SE</td>
<td>880 – 945</td>
</tr>
<tr>
<td>Auropal S</td>
<td>920 – 1060</td>
</tr>
<tr>
<td>Auropal SE</td>
<td>920 – 1060</td>
</tr>
</tbody>
</table>

Figure 3: Ag-Au, Ag-Pd and Au-Pd binary phase diagrams.
Figure 4 shows the optical micrographs of the revealed microstructure for all four investigated dental alloys. The dendritic crystals in the dental alloys of the Midor type are smaller, while the microstructure of the dental alloys of the Auropal type is branched much more dendritically. Dental alloys of the Midor type belong to low carat, as the chemical composition is based on a higher content of Au (40-46 w%), Ag (up to 47 w%), Pd (up to 6 w%) and on the additions of Ir, In and Zn as modifiers, which is reflected by the resulting extremely fine microstructure, where the estimated grain size was around 10 μm. Dental alloys of the Auropal type belong to silver palladium alloys, and have Ag (up to 64 w%) and Pd (up to 25 w%) as their main components. They also contain Au (up to 10 w%). The additions of Cu, Zn, and Au lower the melting point of the dental alloy, and Cu is important because Cu₃Pd is precipitated in the solid phase, which provides the ability to improve these alloys, including homogenisation.18

Table 3: Chemical composition of the cast Ag-Au-Pd-Cu dental alloys (in w%)

<table>
<thead>
<tr>
<th>Ag-Au-Pd-Cu dental Alloy</th>
<th>Au</th>
<th>Pd</th>
<th>Ag</th>
<th>Cu</th>
<th>Zn</th>
<th>Ir</th>
<th>In</th>
</tr>
</thead>
<tbody>
<tr>
<td>Midor S</td>
<td>45.9</td>
<td>6.0</td>
<td>39.5</td>
<td>7.6</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>/</td>
</tr>
<tr>
<td>Midor SE</td>
<td>40.2</td>
<td>4.0</td>
<td>47.0</td>
<td>7.3</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Auropal S</td>
<td>10.3</td>
<td>21.0</td>
<td>58.2</td>
<td>9.5</td>
<td>&lt;1</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Auropal SE</td>
<td>2.0</td>
<td>25.0</td>
<td>64.0</td>
<td>8.0</td>
<td>&lt;1</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

Figure 5: Magnetisation curves [B/H] for dental alloys
The measurements of the chemical composition of the castings using the XRF method showed minimal deviation compared to the nominal chemical composition. The deviation can be attributed to a measurement error of the XRF method (± 10 %), as seen from Table 3.

### 3.2 Magnetic properties

Figure 5 shows the results of the magnetisation measurements for all the tested Ag-Au-Pd-Cu alloys. All the curves revealed that the Ag-Au-Pd-Cu alloys belong to diamagnetic materials, where the magnetic flux density inside is lower than the magnetic flux density outside.

The phenomenon of magnetism relates to the fact that three magnetic moments differ in each atom: the orbital magnetic moment of the electron, the magnetic moment of the spin of the electron and the magnetic moment of the spin of the nucleus. The final magnetic moment of an atom (molecule) is determined by the sum of these three moments, according to the rules of Quantum Mechanics. Therefore, each atom (molecule) can be characterised by only one magnetic moment. In the absence of an external magnetic field, and in the case when the material is not magnetised permanently, the magnetic moments of the atom (molecule) are oriented chaotically, so the magnetisation vector is the same at every point of the material.

When a material appears in a foreign magnetic field, due to the action of magnetic forces, the orientation of the magnetic moments occurs, and, as a result, the magnetisation vector of the material becomes different from zero. In addition to the magnetisation vector, the state of each point of the material in the magnetic view can be described by the magnetic induction vector $B$, and the magnetic field strength vector $H$. At each point of the material between $H$, $B$ and $M$, regardless of whether the material is isotropic or not, and linear or non-linear in the magnetic view, there is a connection:

$$H = B / \mu_0 \approx M$$

where $\mu_0$ is the vacuum magnetic permeability ($\mu_0 = 4\pi \times 10^{-7}$ H/m).

For linear materials, such as diamagnetic and paramagnetic materials, there is a linear relationship between the magnetisation vector at a point and the magnetic field strength vector at the same point:

$$M = X_m \times H$$

where $X_m$ is the magnetic susceptibility of the material.

The magnetic susceptibility of diamagnetic and paramagnetic materials is a scalar quantity (an unnamed number) where these materials are isotropic. In contrast, in ferromagnetic, antiferromagnetic and ferrimagnetic materials, there is no linear dependence between the vectors $M$ and $H$, nor a linear dependence between the vectors $B$ and $H$. The dependences $M = M(H)$ and $B = B(H)$ in ferromagnetic, antiferromagnetic and ferrimagnetic materials are non-linear. Therefore, with these materials, we cannot even talk about magnetic permeability as a permanent characteristic of the material that does not depend on the strength of the magnetic field.

In diamagnetic materials, the magnetic moments of the atoms and molecules of diamagnetic materials are equal to zero in the absence of an external magnetic field. With the presence of an external magnetic field in the atoms and molecules of diamagnetic materials, a magnetic moment is induced, and the material becomes magnetised.

As can be seen in Figure 4, the magnetisation curve for all four Ag-Au-Pd-Cu dental alloys decreased with increasing magnetic field $B$ up to the value of a strong magnetic field of 1 T. Such a magnetic field is very close in value to the powerful permanent magnets or coils used for MR imaging. The earth’s magnetic field is more than 10,000 times smaller than 1 T. The results show that the investigated Ag-Au-Pd-Cu dental alloys manufactured by Zlatarne Celje d.o.o. are non-ferromagnetic, and that they do not pose a risk in MR examinations. This means that Au-Pd dental alloys do not prevent MR examinations, even if the patient has them fixed in the oral cavity. For the purposes of MR examinations, patients who have prosthetic Ag-Pd dental alloy replacements from Zlatarne Celje implanted in their mouths can be issued with an official statement on the non-ferromagnetism of dental alloys, which they should submit to the questionnaire before the MR examination.

### 5 CONCLUSIONS

The study investigated the magnetic properties of four Ag-Au-Pd-Cu dental alloys: Midor S, Midor SE, Auropal S, Auropal SE, which differ in Au content and have a dendritic microstructure after casting. The research showed that Ag-Au-Pd-Cu dental alloys are diamagnetic, which means that the magnetic field density in a substance placed in a magnetic field is slightly less than the magnetic field density outside that substance. This is very important information for users of Ag-Au-Pd-Cu dental alloys in dentistry, where fixed prosthetic structures are manufactured and if an examination with the MR diagnostic method is required, since such a substitute for an MR examination is completely safe for the patient and it is not necessary to remove it.

### Acknowledgment

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### REFERENCES


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