Effect of Platinum Addition to Coinage Metals on Their Ultrasonic Properties

Determination of second- and third-order elastic constants, sound velocity and ultrasonic attenuation

doi:10.1595/147106710X500602 http://www.platinummetalsreview.com/

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Ultrasonic attenuation for the longitudinal and shear waves due to phonon-phonon interaction and due to thermoelastic relaxation mechanisms have been evaluated in bimetallic alloys of the coinage metals (copper, silver or gold) with 1, 2, 3 or 4 at% platinum. The evaluations were carried out along the ⟨100⟩, ⟨111⟩ and ⟨110⟩ crystallographic directions at room temperature. Second- and third-order elastic constants, ultrasonic velocities and thermal relaxation times have also been computed for these alloys. In each case, the addition of platinum to the coinage metal reduces the attenuation, which indicates that bimetallic alloys with a higher platinum content are more ductile and stable and contain fewer defects in their crystal structure than those with a lower platinum content. The predominant mechanism of attenuation of ultrasonic waves is phonon-phonon interaction rather than thermoelastic loss. The results are compared with available theoretical data and experimental measurements for the pure coinage metals. These results, in combination with other well-known physical properties, can be applied to the non-destructive testing of materials for various industrial applications.

Introduction

Ultrasonic non-destructive testing (NDT) is a useful technique that can be applied to a range of materials for the characterisation of their microstructures, the appraisal of defects and the determination of physical properties such as density, thermal conductivity and electrical resistivity. Ultrasonic measurements taken during the fabrication and heat treatment of materials can be used to ensure that the preferred microstructure is obtained and to prevent the formation of defects, including defects in welds between two different alloys. Insight into the interaction of ultrasound with microstructure is also important for resolving many material problems. However, attenuation and backscattering reduce the detectability of defects, especially in platinum alloys with coarse grains or complex microstructures. Therefore it is desirable to minimise attenuation in order to maximise the usefulness of ultrasonic testing.

Information about the microstructure can also be used in material description studies, such as non-destructive determination of grain size. Wave propagation velocity is another key parameter in ultrasonic characterisation and can provide information about crystallographic texture. The ultrasonic velocity, V, is directly related to the elastic constants by the relationship shown in Equation (i):

$$V = \sqrt{(C/\rho)} \qquad \text{(i)}$$

where C is the relevant elastic constant and ρ is the density of that particular material. The elastic constants, in particular, provide valuable information on the stability and stiffness of materials (1, 2).

Physical Properties of Different Alloys

The temperature and magnetic field dependence of the ultrasonic attenuation in rare earth alloys and compounds with crystal-field split energy levels were studied by Becker *et al.* (3). The elastic constants of copper-aluminium alloys were calculated by Soma using a pseudo-alloy-atom model (4). The effects of platinum addition to gold and of indium addition to a gold-platinum alloy on their optical properties were investigated using a computer-controlled spectrophotometer by Shiraishi *et al.* (5). Banhart *et al.* studied the Fermi surface geometry and electrical resistivity of copper-platinum alloys (6). These alloys are particularly interesting because a face centred cubic (fcc) phase exists over the whole range of alloy compositions. Characterisation of gold-silver and gold-copper alloy nanoparticles prepared in chloroform has been done by Kim *et al.* (7).

Gold-platinum alloys (containing ~10% platinum) are of particular interest for their use in dentistry. The biocompatibility and tensile strength of gold-platinum alloys were studied by Hironobu (8). A proposal for the classification of precious metal dental alloys according to their resistance to corrosion based on the ISO 10271 Standard "Dental Metallic Materials – Corrosion Test Methods", 2001, was given by Manaranche and Hornberger (9). Gold- and platinum-based ceramo-metallic alloys were studied by Susz *et al.* to correlate their physical properties to their tendency to release cations (10). Rudolf *et al.* developed the mechanical property and microstructure characterisation of gold-platinum dental alloys (11). These alloys are used in dentistry because of their extremely high chemical stability in the mouth, in addition to desirable mechanical properties such as high strength, ductility and elasticity. Au-Pt-Zn-based alloys have had the advantage of being around for some considerable time. They are part of clinical experience and are extremely successful. The bond between the ceramic and the metal, in particular, is very strong and highly reliable. When considering formulations of Au-Pt-Zn-based alloys for porcelain bonding, high gold contents are required to ensure biocompatibility and large platinum concentrations are necessary to sufficiently raise the melting range above the porcelain firing temperature, to prevent distortion during porcelain application (12, 13).

Ultrasonic Attenuation Studies

Ultrasonic properties have received less attention than other physical properties (14), but progress in materials science means that the study of ultrasonic attenuation now has greater possibilities. Ultrasonic attenuation is related to the thermal conductivity through the thermal relaxation time (15, 16). Investigators have aimed their efforts at explaining the temperature dependence of attenuation in terms of a model in which an ultrasonic phonon interacts with a thermal phonon in the lattice (17–19). All of these studies indicate that the major portion of attenuation is caused by direct conversion of acoustic energy into heat *via* phonon-phonon interaction and through thermal relaxation phenomena. In metals at low temperatures the most important factor contributing to ultrasonic attenuation is electron-phonon interaction. At these temperatures, the electron mean free path increases to the same magnitude as the mean free path of acoustic phonons at high frequency. Hence, the probability of interaction (20) between conducting electrons and phonons increases, as explained by Pippard (21).

The present paper is focused on the ultrasonic study of bimetallic alloys. To the best knowledge of the authors, such studies in the selected alloys have not yet been reported. The selected alloys are (in at%): copper-platinum ($Cu_{100-x}Pt_x$), silver-platinum ($Ag_{100-x}Pt_x$) and gold-platinum ($Au_{100-x}Pt_x$), where in each case x = 1, 2, 3 or 4. These alloys all have an fcc structure. Ultrasonic velocities, attenuation and thermal relaxation time are evaluated in these compounds along the crystallographic directions ⟨100⟩,

⟨110⟩ and ⟨111⟩ at room temperature. The second-order elastic constants (SOEC) and third-order elastic constants (TOEC) are also calculated using the Born-Mayer model (22, 23).

Second- and Third-Order Elastic Constants

The Coulomb and Born-Mayer potentials are applied to evaluate the SOEC and TOEC (22). The elastic constants are then used to compute ultrasonic parameters such as ultrasonic velocity, thermal relaxation time and the acoustic coupling constants. These parameters are used in turn to evaluate ultrasonic attenuation. All the equations used to compute the SOEC and TOEC of these alloys are presented in our previous paper (23).

The SOEC and TOEC are calculated from the nearest neighbour distance, r_0, (24). These are given in Table I. The hardness parameter, b, (25) for each alloy is 0.315 Å. The SOEC and TOEC of the (Cu, Ag or Au)-Pt alloys as obtained from the Coulomb and Born-Mayer potentials up to the second nearest neighbour are presented in Table II.

Published experimental data on the elastic constants for the chosen alloys are not available for comparison. Comparison of the present values to

Table I

Values of the Nearest Neighbour Distance, r_0, for Bimetallic Alloys of the Coinage Metals with Platinum

Alloy composition, at%	Nearest neighbour distance, r_0, Å
$Cu_{99}Pt_1$	2.5621
$Cu_{98}Pt_2$	2.5642
$Cu_{97}Pt_3$	2.5663
$Cu_{96}Pt_4$	2.5684
$Ag_{99}Pt_1$	2.889
$Ag_{98}Pt_2$	2.880
$Ag_{97}Pt_3$	2.89
$Ag_{96}Pt_4$	2.885
$Au_{99}Pt_1$	2.888
$Au_{98}Pt_2$	2.887
$Au_{97}Pt_3$	2.886
$Au_{96}Pt_4$	2.885

Table II

Second- and Third-Order Elastic Constants of Bimetallic Alloys of the Coinage Metals with Platinum at 300 K

Alloy	Second-order elastic constants, 10^{10} N m^{-2}			Third-order elastic constants, 10^{10} N m^{-2}					
	C_{11}	C_{12}	C_{44}	C_{111}	C_{112}	C_{123}	C_{144}	C_{166}	C_{456}
$Cu_{99}Pt_1$	6.957	2.002	2.298	–100.5	–8.362	2.267	3.713	–9.447	3.632
$Cu_{98}Pt_2$	6.784	1.995	2.285	–98.85	–8.344	2.254	3.699	–9.378	3.620
$Cu_{97}Pt_3$	6.717	1.986	2.275	–98.21	–8.309	2.241	3.687	–9.332	3.608
$Cu_{96}Pt_4$	6.679	1.978	2.265	–97.84	–8.273	2.229	3.675	–9.291	3.596
$Ag_{99}Pt_1$	5.821	1.081	1.347	–90.57	–4.401	0.722	2.304	–5.471	2.253
$Ag_{98}Pt_2$	5.694	1.078	1.346	–89.22	–4.372	0.719	2.301	–5.482	2.250
$Ag_{97}Pt_3$	5.652	1.083	1.347	–88.76	–4.411	0.723	2.307	–5.473	2.256
$Ag_{96}Pt_4$	5.632	1.085	1.349	–88.55	–4.419	0.729	2.310	–5.478	2.259
$Au_{99}Pt_1$	5.250	1.131	1.374	–79.41	–4.664	0.955	2.303	–5.619	2.250
$Au_{98}Pt_2$	5.140	1.132	1.372	–78.29	–4.679	0.960	2.304	–5.604	2.251
$Au_{97}Pt_3$	5.104	1.134	1.374	–77.92	–4.689	0.960	2.307	–5.608	2.555
$Au_{96}Pt_4$	5.551	1.126	1.387	–82.35	–4.588	0.954	2.316	–5.693	2.258

theoretical and experimental studies of pure metals, as shown in Table III, demonstrates that results obtained from the present investigation are lower than those of the pure metals as reported by other investigators (26, 27). The values of the elastic constants show that the crystals are elastically stable, since the stability conditions: $C_{44} > 0$, $C_{11} > 0$, and $C_{11} > C_{12}$ are satisfied. The elastic constants also indicate that thermal softening occurs as the platinum content in each alloy is increased. The obtained values of the SOEC and TOEC are of the same order as previous experimental and theoretical studies of metallic alloys and metals (14, 27). Therefore we conclude that our theoretical approach to evaluate the SOEC and TOEC is valid for the selected bimetallic alloys.

Ultrasonic Attenuation and Related Parameters

The most important causes of ultrasonic attenuation in metallic alloys are phonon-phonon interaction and the thermoelastic mechanisms at room temperature. Expressions for calculating ultrasonic attenuation and related parameters are given in our previous papers (16, 28).

Ultrasonic velocities for the longitudinal wave, V_L, and the shear wave, V_S, together with the Debye average velocity, V_D, of the chosen alloys are plotted in Figure 1. The thermal conductivity of the alloys is taken from previously published values (29). Total attenuation, $(\alpha/f^2)_{Total}$, is given by (Equation (ii)):

$$(\alpha/f^2)_{Total} = (\alpha/f^2)_{Th} + (\alpha/f^2)_L + (\alpha/f^2)_S \qquad \text{(ii)}$$

where $(\alpha/f^2)_L$ is the ultrasonic attenuation due to phonon-phonon interaction for the longitudinal wave; $(\alpha/f^2)_S$ is that for the shear wave; $(\alpha/f^2)_{Th}$ is that due to thermal relaxation; α is the ultrasonic attenuation coefficient and f is the frequency. Thermal conductivity, k, thermal relaxation time, τ, and total attenuation along the $\langle 100\rangle$, $\langle 110\rangle$ and $\langle 111\rangle$ orientations are presented in Figures 2 and 3 for the copper, silver and gold alloys. It can be seen from Figure 1 that, as we increase the platinum content of the alloys, the ultrasonic velocities change slightly due to a change in the elastic constants. Wave velocities are highest for the Cu-Pt alloys and lowest for the Au-Pt alloys. Based on wave velocity, Cu-Pt alloys may prove to be more workable than the other alloys in this study, and therefore more suitable for further investigation into potential industrial applications than the Ag-Pt or Au-Pt alloys. The wave velocity of these compounds is useful for finding their anisotropic properties. The order of velocities in the present case is

Table III

Second-order Elastic Constants and Bulk Modulus of Selected Bimetallic Alloys of the Coinage Metals with Platinum Compared to Pure Metals at 300 K

Material	Second-order elastic constants, 10^{10} N m^{-2}			Bulk modulus, 10^{10} N m^{-2}
	C_{11}	C_{12}	C_{44}	B
$Cu_{99}Pt_1$	6.96	2.00	2.30	5.38
Cu (experimental) (26)	17.62	12.49	8.17	13.70
Cu (27)	13.61	11.98	6.65	12.53
$Ag_{99}Pt_1$	5.82	1.08	1.35	3.74
Ag (experimental) (26)	13.15	5.73	5.11	10.07
Ag (27)	8.82	7.91	4.42	8.20
$Au_{99}Pt_1$	5.25	1.13	1.37	3.58
Au (experimental) (26)	20.16	16.97	4.54	17.32
Au (27)	15.00	12.86	7.03	13.57

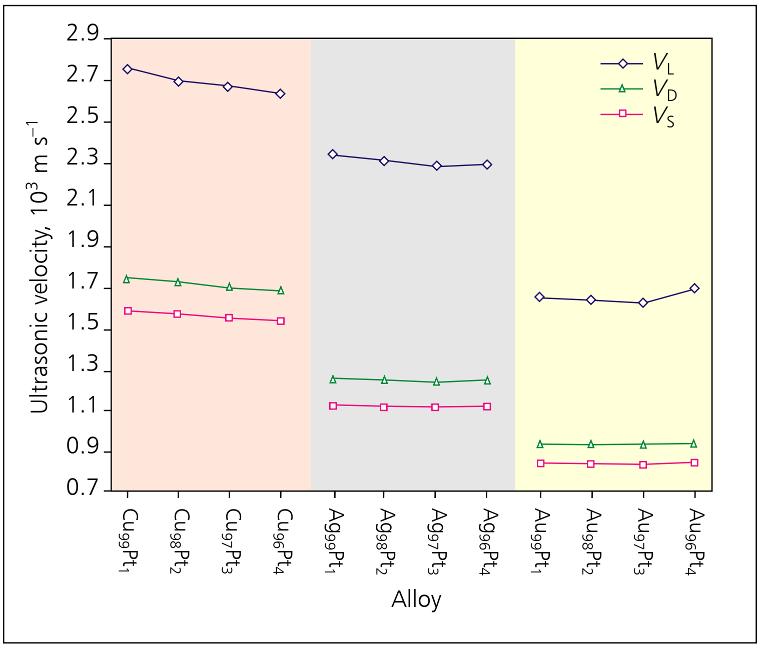

Fig. 1. Ultrasonic velocity for bimetallic alloys of the coinage metals copper, silver or gold with platinum. V_L = ultrasonic velocity for the longitudinal wave, V_S = ultrasonic velocity for the shear wave, V_D = Debye average velocity

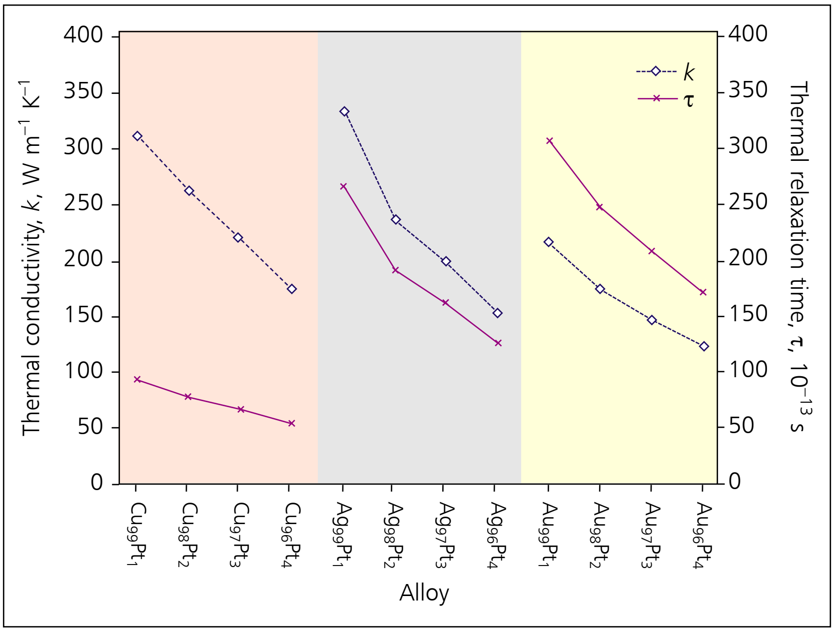

Fig. 2. Thermal conductivity, k, (in W m^{-1} K^{-1}) and thermal relaxation time, τ, (in 10^{-13} s) for bimetallic alloys of the coinage metals copper, silver or gold with platinum

found in the same way as for an earlier study (15). The thermal relaxation time of these alloys is of the order of 10^{-11} s, which is as expected for pure metals and alloys (14, 30).

Figures 2 and 3 show that ultrasonic attenuation follows the decreasing trends in thermal conductivity and thermal relaxation time with increasing platinum content in these alloys. This is expected since the ultrasonic attenuation, α/f^2, is proportional to the thermal relaxation time, τ, and the acoustic coupling constant, D; and τ is proportional to the thermal conductivity, k. Although a large number of physical parameters are involved in calculating ultrasonic attenuation, Figures 2 and 3 show that total attenuation along each orientation follows the same trend as the thermal relaxation time and the thermal conductivity along the same orientation. The thermal relaxation time gives the collective effect of thermal conductivity, specific heat per unit volume, C_V, and Debye average velocity, V_D.

It can also be seen from Figure 3 that the total attenuation in the Cu-Pt alloys is low in comparison to that in the Ag-Pt and Au-Pt alloys. The Cu-Pt alloys have the fewest defects in their crystal structure at room temperature, while the Ag-Pt and Au-Pt alloys may have more defects at room temperature and have greater attenuation. In all of the alloys, ultrasonic attenuation due to the thermoelastic relaxation process is negligible, at approximately 0.2% to 0.5% of the total attenuation, while attenuation due to the phonon-phonon interaction mechanism is greater than 99% of the total. Hence, ultrasonic attenuation due to phonon-phonon interaction is the predominant component of attenuation in these materials.

From Figure 3, it is very clear that as platinum content is increased in these alloys, attenuation decreases. Hence the platinum is playing a critical role in these compounds. Because no experimental data for the chosen alloys are available for comparison, we have compared our results with data for pure copper, silver and gold. The calculated value of ultrasonic attenuation for the longitudinal wave along the ⟨100⟩ direction is 59 × 10^{-15} Np s^2 m^{-1} for $Cu_{99}Pt_1$, while the experimental value of attenuation in pure Cu is 97 × 10^{-15} Np s^2 m^{-1} along the ⟨100⟩ direction (30), and attenuation in pure Pt along this orientation is much lower at about 6.25 × 10^{-16} Np s^2 m^{-1} (31). So it is clear that Pt has advantages in comparison to Cu for aspects like ductility and stability. The selected Cu-Pt alloys have lower attenuation than the Ag-Pt and

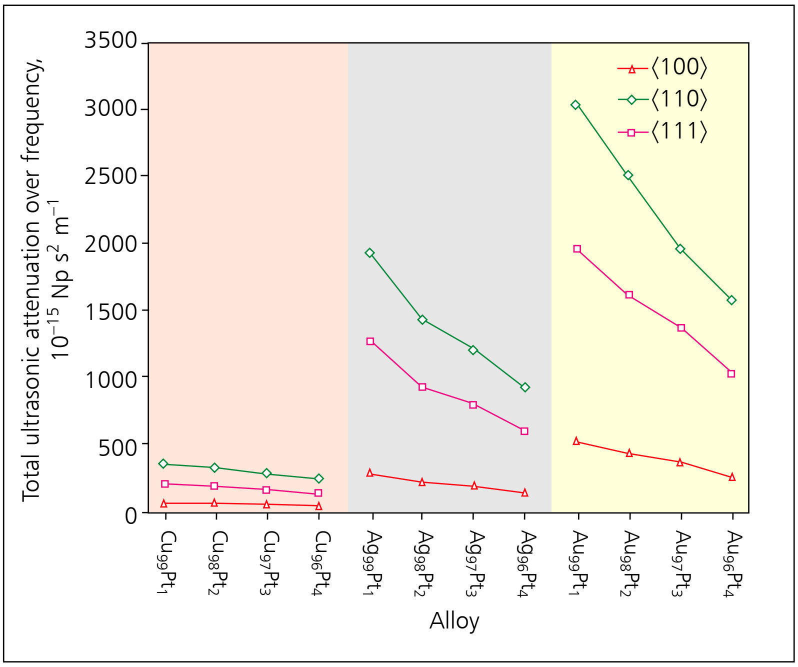

Fig. 3. Total ultrasonic attenuation over frequency (in 10^{-15} Np s^2 m^{-1}) for bimetallic alloys of the coinage metals copper, silver or gold with platinum

Au-Pt alloys. Hence the Cu-Pt alloys are expected to be more ductile, stable and contain fewer defects in their crystal structure. This type of ultrasonic attenuation behaviour is in accordance with the fact that ultrasonic attenuation is inversely proportional to ultrasonic velocity to the power of 3/5, and this explains the calculated attenuation behaviour presented here. This is also a confirmation of the present theoretical approach.

Conclusions and Scope for Future Work

This paper compares calculated values of the second-order elastic constants for the selected bimetallic alloys with experimental values for the pure coinage metals. The ultrasonic velocities for the longitudinal and shear waves increase with increasing magnitude of the elastic constants, and in this study are higher in the copper-platinum alloys than in the silver-platinum or gold-platinum alloys. The thermal relaxation time, τ, decreases with increasing platinum content in the alloys studied. The ultrasonic attenuation is also shown to decrease with increasing platinum content in these bimetallic alloys. Based on these results, $Cu_{96}Pt_4$ is expected to be more ductile and stable and contain fewer defects in its crystal structure than the other alloys included in this study. On the basis of our results, $Cu_{96}Pt_4$ may prove to be more workable than the other alloys in this study and is therefore recommended as a suitable material for further investigation into potential industrial applications. The preliminary results obtained in this work can be used for further experimental investigation with the pulse echo overlap (PEO) technique for ultrasonic measurements, and with conventional analytical techniques such as polarising microscopy, X-ray diffraction (XRD), surface tension analysis, solid state nuclear magnetic resonance (NMR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

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