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Electromechanical polishing of alloys of copper and gold with the transition metals of the first long period

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The electromechanical polishing of binary alloys of copper and gold with the Periodic Table elements from Ti to Se inclusive has been investigated with special reference to the inter-relation between the polishing response and the systematics of alloying behaviour. The electrolyte contained 12 wt % sodium thiosulphate with varying additions of potassium thiocyanate. Wide ranges of composition of primary solid solution of the transition metals and B Group elements in copper and gold, and also a few chromium- and vanadium-base alloys, polish satisfactorily. Brief mention is also made of the polishing of Ag–Al alloys and Fe–Mn–P–C metallic glasses.

1. Introduction

No method of metallographic polishing can rival, for versatility, the traditional mechanical polishing wheel, nowadays usually loaded with diamond dust as an abrasive. There are however several ancillary methods, each with its specialist features and range of applicability. Electromechanical polishing is one of these [1, 2], and it is particularly useful for the metals and alloys of those transition elements which have full or nearly full d-shells. The elements which are polished by the particular electrolyte used herein are indicated in Table I. Use of other electrolytes expands the range, though, in the author's experience, not greatly. The polishing of B Group elements has been briefly recorded [3], but alloys based on these are not discussed subsequently.

Some results on copper–nickel, copper–manganese and gold–iron alloys [4] proved so interesting that it was decided to extend them into a systematic survey of the polishing of alloys of copper and gold, separately, with the 3d transition elements. There were two objectives in mind. The first was the practical one of simply determining the limits of applicability of a particular electrolyte. The second will be perhaps apparent from Table I where the strong correlation in the Periodic Table poses the question as to how these limits are related to some other properties of the elements and their solid solutions.

TABLE I Elements which are polished by the electromechanical technique using thiosulphate-base electrolytes, arranged as in the Periodic Table

V	Cr	–	–	–	–	Cu	Zn	–	–	–	–
–	–	–	–	–	Pd	Ag	Cd	In	Sn	Sb	Te
–	–	–	–	–	–	Au	–	Tl	Pb	Bi	–

Note: (a) Polishing of palladium is very slow; (b) The results of polishing action on Zn, Cd and In were inferior to those on other elements.

2. Experimental method

Most of the samples were produced as arc-melted small buttons (copper-base 1 to 2 g; gold-base 0.2 to 0.5 g), but a few alloys with B Group elements were produced, also by direct synthesis, in evacuated quartz capsules, in each case from high-purity materials [5]. Compositions are in atomic per cent.

Samples were tested as-cast, except where otherwise stated. They were mounted in copper-loaded thermoplastic resin (Struers) and ground down, finishing on 600 grit paper, prior to polishing. The specimen was made anode, and no alumina was added to the electrolyte, mechanical action being therefore confined to rubbing from the (cotton-type) cloth. The electrolyte contained 12 wt % sodium thiosulphate crystals with 19 wt % potassium thiocyanate. However, a solution of

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thiosulphate without the thiocyanate was used for pure copper and nearly related compositions. The current necessary was of the order of a few hundred milliamps, though this may be reduced for high-copper content alloys.

The overall picture, therefore, is that, as one moves away from pure copper in the Periodic Table, increase of thiocyanate and current becomes necessary, and this variability is implicit in what follows, so that detailed conditions are not quoted. The electrolyte is generally quick-acting (about half a minute), so that re-grinding and optimizing of conditions are simple to effect.

3. Results and discussion

Before discussing the results, it will be helpful to consider the broad pattern of alloying behaviour of the coinage metals with the elements from titanium to selenium, inclusive. In order to be able to condense a great deal of information, we make use of synoptic diagrams of the type shown in Figs 1 and 2 (copper-base and gold-base, respectively). The method of representation, used by Brewer [6] and, with hyperbola grid additions, by Stone [7], is described thus. The left-hand edge represents the elements of the First Long Period, so that, for example, nickel–copper alloys of different compositions are represented by points on a horizontal tie-line from "Ni", to the right-hand side. For copper–cobalt and copper–iron alloys there are extensive ranges of insolubility, and in Fig. 1 a closed curve has been drawn through points representing the maximum solubilities. Similar curves have been inserted elsewhere in

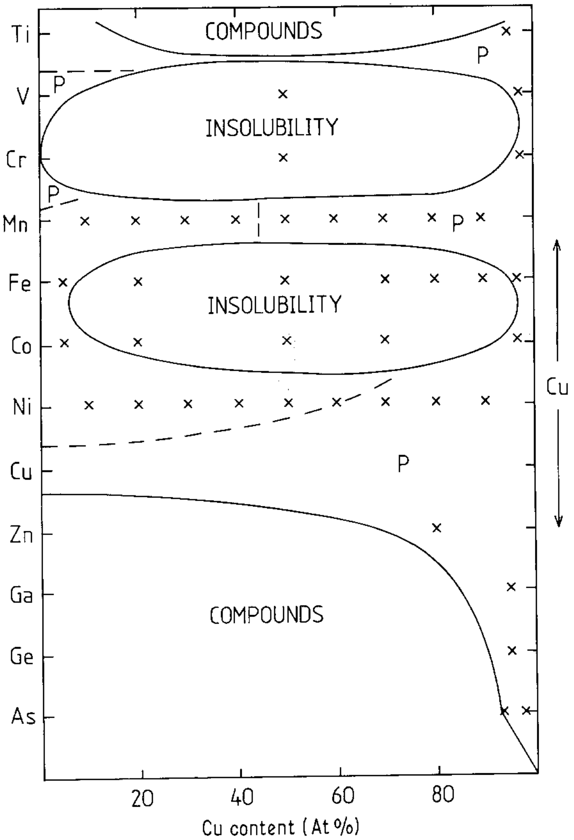

Figure 1 Synoptic diagram showing (a) the phase constitution in outline of systems of the elements titanium to selenium inclusive with copper, and (b) zones (P) where alloys are polished electromechanically. Note that compositions prepared and tested are indicated by crosses; for clarity no markings are inserted for the pure elements. Many commercial brass-type alloys have also been polished.

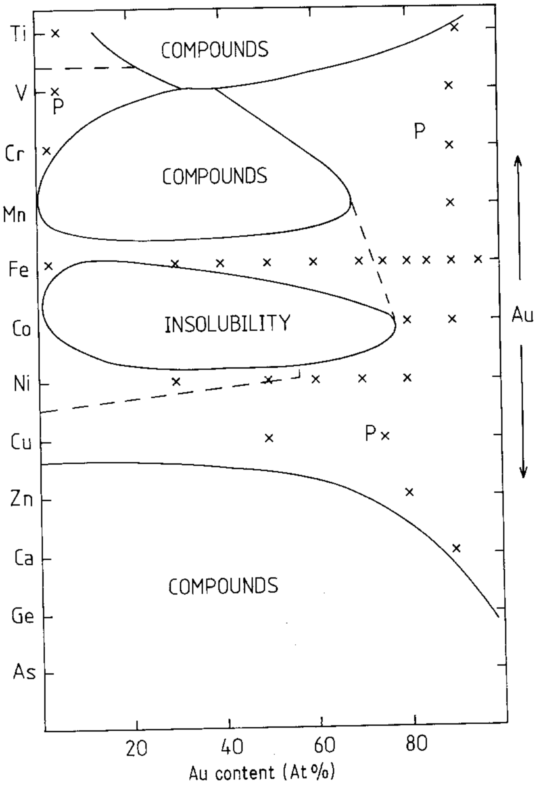

Figure 2 Synoptic diagram showing (a) the phase constitution in outline of systems of the elements of the Periodic Table from titanium to selenium inclusive with gold, and (b) zones (P) where alloys are polished electromechanically. The sources for data on phase equilibria were Hansen *et al.* [9], and Moffatt [10] for more recent data on the Au–V system. The intermediate zone of composition indicated for systems with V, Cr and Mn should possibly be broken into two or alternatively labelled "compounds/insolubility", but in view of uncertainties the present labelling is preferred. Superlattices are counted as solid solutions. Extensive ranges of superlattice stability occur in Au–3d systems.

Figs 1 and 2, though at low (Ti) and high (Zn to Se) atomic numbers the insolubilities are derived from the existence of intermetallic compounds. The particular form of the solubility curve for B Group elements in copper may be understood in terms of a recent hypothesis [7]. A single "insoluble" closed curve sketches the equilibria around copper–Group VIA, but conditions for gold-base alloys are more complicated, though it is clear that primary solubilities are limited. The solubility gaps half-way along the 3d series (Figs 1 and 2) are of some interest, that is, solubilities are greatest along a manganese–copper tie-line (Fig. 1) and iron–gold tie-line (Fig. 2). This is consistent with an interpretation of solubilities as due to equal contributions to the flux of valency electrons if a half-filled d-shell is assumed (i.e., manganese plus divalent copper, gold plus trivalent iron). In silver-3d systems the insolubility loops with the transition elements are subsumed in one much larger insolubility zone, consistent with incompatibility from univalent silver.

The crosses in Figs 1 and 2 indicate the compositions tested. As a result of the findings of the polishing tests on these, dashed lines have been added in order to help summarize the results. They are placed in such positions that, in conjunction with parts of the full lines, the limits of polishing are indicated. Thus, dashed lines are marked (a) from the left-hand edges from between "Cu" and "Ni", (b) in mid-diagram between the insolubility loops, and (c) near "Cr". The locations of polishing zones are given by markings "P". By these means the essential findings of the paper are presented. Supplementary notes are given in the following paragraph.

A copper alloy with 50 at % manganese was polished, but a copper alloy with 60 at % manganese was not, and this limit did not seem to be much influenced by heat-treatment. On the other hand, the polishing limit in gold–iron alloys is increased from about 25 at % (Fig. 2) to 60 at % by solution-treatment followed by water-quenching. High nickel-content copper–nickel alloys, and also iron and cobalt with and without copper, suffered some variable pitting attack without any polishing action. Manganese-rich samples were attacked by the solution without application of e.m.f., giving a brown discoloration. Chromium- and vanadium-rich alloys polish slowly, with a yellow colouring in the case of vanadium; titanium is coloured yellow but no polishing takes place. There is some evidence that polishing of chromium is increased, if indeed it is not made possible, by increase in oxygen content. The samples of alloys from the Cu–Co and Cu–Fe insoluble phase fields broke up fairly vigorously, and subsequent thorough washing of the cloth was necessary. The polishing behaviour of gold-containing alloys was generally similar to the copper-base, but a constitutional difference exists in that there is solid immiscibility in the gold–nickel system. However, simple magnet tests on the tiny (and therefore quickly cooled) samples were consistent with the probability that the metastable disordered solid solution was present. Silver-base alloys were not studied in detail, but it has been found that pure silver and silver-rich silver–manganese alloys may be polished under conditions similar to the present.

Apart from the polishing zone near "Cr" in Figs 1 and 2, a feature which, as already indicated, may be linked with oxygen content, the broad conclusion is that polishing is possible for all the copper- and gold-rich solid solutions with the 3d elements. The limits of polishing coincide with limits of solubility, with two exceptions. Firstly, in the Cu–Mn (Fig. 1) and Au–Fe (Fig. 2) systems, the practical limits may well be connected with increasing instability, with decrease of temperature, of the α-solid solution. The limit of polishing between 40 and 50 at % Ni in the copper–nickel system is more difficult to understand, in view of the extensive solid solutions. It may be connected to a crossover in the electronic constitution, which may be expressed in terms of a hypothesis of s–d resonance [8], using an argument as follows.

The electronic structure of solid copper and nickel (the electron occupancy probabilities) may be indicated by the band-box (i.e., mixed band–spin-box) method, as in Fig. 3. Here the structure of the copper with a full d-shell and one s-electron is suggested in the upper part, and that of nickel, with 0.62 s-electrons and a corresponding "hole" in the d-shell, below it. Resonance of the s–d type may be represented by the arrows from s-states into the d-shells of neighbouring atoms of the other species. It will be seen that the crossover from Cu–Cu to Ni–Ni interactions with increasing nickel content takes place at a concentration represented by the intersection of the two arrows, expressed as a percentage of the distance from "Cu" to "Ni". From the geometry, this distance must be divided in the ratio $1.0:2 \times 0.62$, which gives the crossover at 44.7 at % nickel. This is in

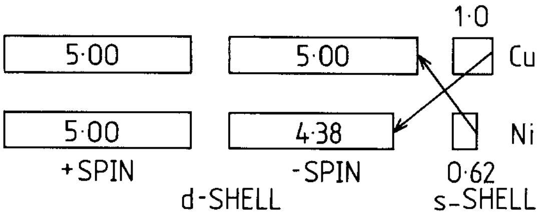

Figure 3 Resonance between copper and nickel atoms in Cu–Ni alloy. Note: (a) For clarity Cu–Cu and Ni–Ni interactions are not shown; (b) The crossing of the arrows does not imply that resonance is necessarily mutual and synchronous; (c) A similar argument may be used for the composition of the onset of ferromagnetism in Cu–Ni alloys.

reasonable agreement with the data on Fig. 1, considering that the alloys were as-cast. As to what may happen at the polishing interface at crossover, it is possible that the electrolytic process attempts to pump-in "integral" electrons, as for copper, the higher-nickel alloys cannot accept this, and the surface breaks up with the resulting stress. (The interface is surely especially clean in this method of polishing, in marked contrast with the more conventional electrolytic polishing electrolytes which rely on a viscous layer.)

Since the work for this paper was conducted some results on two other types of alloy system have been reported. The first relates to experiments on silver–aluminium alloys. The above work does not consider what happens beyond the α-phase solubility limit of copper and gold alloys with B Group elements although, obviously, if some of the alloys had contained intermediate phase, this would have been taken into account in assessing the results. The picture, so far as could be seen, was of either slow polishing, or no polishing, beyond the α-phase limit. For example, observations on copper–zinc alloys showed that the β-phase is smoothed but not (bright) polished, whilst the γ-phase is inert; in the cooper–arsenic system, an alloy with overall arsenic content near the solubility limit was inert. The silver–aluminium system is interesting because the first intermediate phase field, ζ, extends from 24 to 42 at % Al and the range includes the electron–atom ratios of 3:2 and 7:4. Experiments with the present technique apparently show that alloys with 20 and 30 at % Al may be polished, and that part of the structure of a 40 at % Al alloy is polished. The second type of substance was a series of metallic glasses in the form of quenched ribbons of composition (Fe, Mn)PC, with phosphorus and carbon held at 16 and 4 at %, respectively. The metallic content ranged from 100 at % iron to 20 at % iron, balance manganese. Room-temperature ferromagnetism did not exist above about 17 at % replacement by manganese. In contrast to the results on crystalline alloys, it was found that compositions with high-iron content could be polished. The composition limit for polishing was approximately 50% replacement, and the reflectivity of as-polished samples was not so high.

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