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Electrical and Tensile Properties of Cu-ThO_2, Au-ThO_2, Pt-ThO_2 and Au-Al_2O_3, Pt-Al_2O_3 Alloys

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Dispersion-strengthened alloys of Pt, Au and Cu containing ThO_2 and Al_2O_3 were prepared by precipitating the elements from a solution containing a suspension of the oxide phase. The precipitate deposited on the oxide particles of 0.05 μm average diameter and produced dispersions of good homogeneity on compaction. Alloys containing less than 2 vol % oxide phase had sufficient ductility to permit fabrication of wire. Tensile strength and elongation, hardness, and electrical resistivity were measured as a function of temperature up to 1000°C. The dispersion-strengthening caused a relatively small increase in the resistivity of the alloys compared to the resistivity of the metals. The alloys are useful where high electrical or thermal conductivity combined with superior tensile strength, hardness and oxidation resistance at elevated temperatures, are desirable.

1. Introduction

When a finely divided second phase is distributed in a metallic crystalline matrix, an alloy is formed which is stronger than the matrix phase. These alloys are termed *dispersion-strengthened* or *dispersion-hardened* alloys. Some of the technical applications for these materials have been described by Ault and Burte [1]. The dislocation mechanisms responsible for the improved strength, hardness and creep resistance of dispersion-strengthened alloys have been reviewed by Ansell [2]. In general, the yield strength of a dispersion-strengthened alloy is approximately inversely proportional to the interparticle spacing for fine dispersions and inversely proportional to its inverse square root for coarse particles [2,3]. In practice, in order to optimise strength and ductility, it is necessary to use a uniform and homogeneous dispersoid of low volume fraction and small particle size which is stable in the metallic matrix.

In this paper we report on a new technique for preparing dispersion-strengthened alloys and investigate the electrical resistivity, tensile and yield strength, ductility and hardness of alloys of Cu, Au and Pt with ThO_2 and Au and Pt with Al_2O_3.

In order to obtain a more uniform distribution of individual dispersoid particles in the metallic matrix, metal was plated on the individual particles by *chemical plating*. The particles were vigorously agitated by mechanical and/or ultrasonic stirring to avoid particle clustering. Chemical plating of ThO_2 and Al_2O_3 dispersoid particles of less than 0.05 μm average diameter used in this investigation was achieved by suspension of the particles in an agitated aqueous solution of a metal salt, which is then chemically reduced by the addition of a reducing agent. The metal precipitates onto the individual dispersoid particles. The resulting powder is dried and outgassed, pressed, extruded, heat treated and worked by normal powder metallurgical techniques to form specimens of dispersion-strengthened ingots or wires. Better dispersoid uniformity, homogeneity and mechanical properties can be obtained using this technique than with the usual mechanical mixing of dispersoid and metal powders [4]. It is also demonstrated that considerable improvement in room temperature and elevated temperature mechanical properties are achieved with relatively small increases in the electrical and thermal resistance. This result is not surprising since an increase in resistivity over and above the volume-effect increase should be due to internal surface or boundary scattering

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of electrons, which is a relatively weak scattering mechanism in macroscopic specimens. These properties are useful in many electronic, electrical and thermal applications, especially those involving elevated temperatures. Other strengthening mechanisms, such as solid-solution and work-hardening, anneal out at higher temperatures and the former produces large increases in resistivity for a given mechanical property improvement.

2. Theory

2.1. Tensile

The initial yield stress, τ, of a fine-particle dispersion-strengthened alloy can be estimated by the modified Orowan relation of Kelly and Nicholson [2, 5].

$$\tau = \tau_S + Gb\phi/2\pi(S - d_S)\, ln \left(\frac{S - d_S}{2b}\right) \quad (1)$$

where τ_S = yield stress of the matrix; d_S = mean planar particle diameter of dispersoid = $(2/3)^{1/2}\bar{d}$ where $\bar{d}$ = median diameter, S = mean planar interparticle spacing of the dispersion = $0.25\pi^{1/2} d_S/f^{1/2}$, f = volume fraction of dispersoid, G = shear modulus of the matrix, b = dislocation vector of the matrix, and $\phi = [1 + 1/(1 - \nu)]$, where ν is Poisson's ratio. Thus, the strengthening improves as the particle size decreases. As the volume fraction, f, of dispersoid increases, the yield strength increases but the ductility decreases [2].

2.2. Electrical

As long as the electronic mean free path (mfp), l_0, in the matrix material is a small fraction of the distance, S, between dispersoid boundaries, the presence of these boundaries should not significantly change transport properties of the metallic matrix. Increasing the volume fraction, f, of dispersoid until the distance between internal boundaries, S, begins to approach the mfp l_0 will cause a significant fraction of the conduction electrons to be scattered by the dispersoid surface rather than by electrons and phonons in the matrix. This will augment the matrix relaxation mechanisms and diminish the effective mfp. If the surface-scattering and matrix or bulk relaxation mechanisms are assumed statistically independent [5], then

$$l^{-1} = l_0^{-1} + l_S^{-1} \quad (2)$$

where l_0 and l_S are the matrix mfp and the mfp associated with surface scattering respectively. Dingle [6] and Blatt [7] have shown that the resistivity ρ of a thin film or wire of thickness or diameter d in the limits $d \gg l_0$ and $d \ll l_0$ reduces to

$$d \gg l_0 : d \ll l_0:$$

$$\text{(FILM)}\quad \rho = \rho_b \left(1 + \frac{3}{8}\frac{l_0}{d}\right)$$

$$\rho = \rho_b \left[\frac{4}{3}\frac{l_0}{d}\left(ln\, \frac{l_0}{d}\right)^{-1}\right] \quad (3)$$

$$\text{(WIRE)}\quad \rho = \rho_b \left(1 + \frac{3}{4}\frac{l_0}{d}\right)$$

$$\rho = \rho_b \frac{l_0}{d} \quad (4)$$

where ρ_b is the bulk resistivity and the magnetic field is zero. Applying these equations to a dispersion-strengthened matrix with volume fraction f dispersoid of less than 0.05, the effects of surface-scattering on dispersoid particles of size of the order of 500 Å separated by distances, S, greater than 5000 Å is clearly negligible at room temperature and above. However, at very low temperatures the effect of surface-scattering on the resistivity of the alloy should be observed if the conduction electron mfp l_0 approaches the mean particle-spacing S.

3. Preparation of Dispersion-Strengthened Alloys

3.1. Copper Alloys

Copper-thoria alloy powders were prepared by precipitating copper metal from dilute solution of copper acetate containing a suspension of thoria powder.

Cupric acetate monohydrate ($CuC_2H_3O_2.H_2O$) was dissolved in hot distilled water. To obtain a pound (454 g) of copper metal, 1400 g of cupric acetate monohydrate were added to 10 litre of hot (75° C) distilled water. The solution was stirred vigorously with a mechanical stirrer and 6 N ammonium hydroxide was added to complex the copper solution. For 1400 g of cupric acetate monohydrate 100 ml of 6 N ammonium hydroxide was used. The desired amount of 0.05 μm diameter thoria powder was weighed and added to the mechanically stirred solution.

In order to precipitate the copper onto the thoria powder a 50% hydrazine (N_2H_4) solution (250 ml for 1400 g of cupric acetate monohydrate) was added dropwise to the heated (60° C) and stirred solution containing the suspension of thoria particles.

The precipitate was filtered and dried in a

TABLE I Fabrication parameters for dispersion strengthened alloys

Alloy	Degassing temperature (°C) (dry H_2)	Final reduction method	Final size (thickness or diameter) (cm)	Amount of C.W., %
Cu Alloys:				
Cu-2.2 vol % ThO_2	800	Cold-swaging	0.175	50
Cu-5.0 vol % ThO_2	650	Hot-swaging (700°)	0.25	0
Au Alloys:				
Au-3.5. vol % Al_2O_3	Not degassed	Cold-rolling	0.025	60
Au-3.4 vol % ThO_2	650	Cold-rolling	0.025	50
Au-6.4 vol % ThO_2	650	Cold-rolling	0.025	50
Pt Alloys:				
Pt-1.8 vol % Al_2O_3	800	Cold-rolling	0.025	50
Pt-1.0 vol % ThO_2	1000	Cold-swaging	0.175	70
Pt-1.8 vol % ThO_2	1300	Cold-rolling	0.025	60

vacuum oven (10^{-3} torr) at 50° C. These powders were prepared for fabrication into ingots or wire for property measurements, by first degassing in a dry hydrogen furnace for 4 h at the temperatures shown in table I. This treatment was necessary for reduction of any copper oxide formed in the previous process. Powders not degassed before fabrication yielded fabricated products which blistered when heated after fabrication.

The degassed powders were pressed in steel dies at 200000 psi and sintered in dry hydrogen at 900° C for 1 h. The sintered slugs of copper were canned for extrusion in a copper can. The canned slugs were evacuated, heated to the extrusion temperatures and sealed off just before extrusion. Extrusions were made at approximately 600° C with a 25:1 reduction in area. The copper cladding was removed by dissolving in nitric acid. Further reduction to wire was achieved by swaging. Alloys containing 5 vol % of the oxide phase could not be cold-swaged without cracking; hot-swaging of these alloys met with only marginal success owing to cooling of the rods by the swaging dies. The swaging of the lower volume fraction (2.2 vol %) oxide alloys was accomplished by cold-swaging through a series of dies, each effecting a 5% reduction in area. The rods or wires were annealed between each swaging pass at 800° C. The 2.2 vol % alloy was given a final 50% reduction-in-area cold-swaging treatment to give a cold-worked structure.

Samples of the hydrogen-reduced powders were mounted in epoxy resin and examined metallographically by replica electron microscopy. Cellulose acetate two-stage replicas were made of the dispersion-hardened material after etching with aqua regia diluted in glycerine. Fig. 1 shows a sample of loose powder of Cu-5-vol % ThO_2 after hydrogen reduction at 1000°C for 3h. The particle homogeneity is excellent. Similar results were obtained for the other Cu alloys.

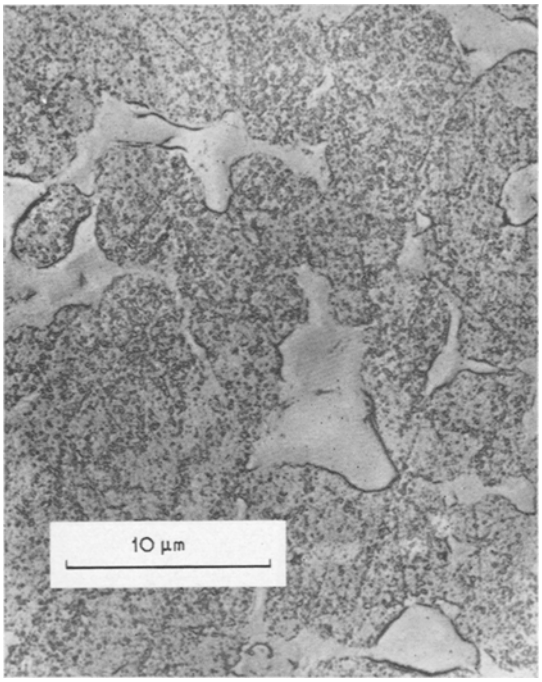

Figure 1 Electron micrograph Cu-5 vol% ThO_2 loose powder gravity-packed and heated to 1000° C for 3 h in H_2. (The large white areas are packing cavities).

Examination of extruded samples heated in a vacuum-furnace for 40 h at 1000° C showed no apparent growth of the thoria particles.

3.2. Gold Alloys

The gold alloys were prepared by first dissolving gold in aqua regia to form a solution of gold

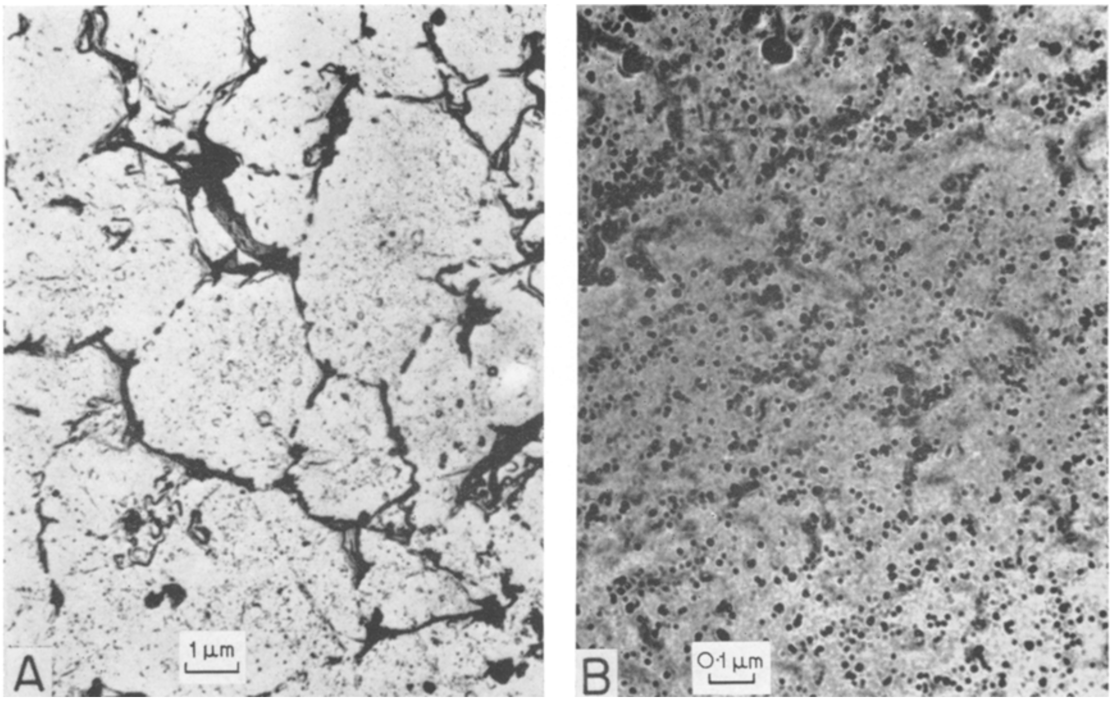

Figure 2 Electron micrograph Au-3.5 vol% Al$_2$O$_3$ at two magnifications shown.

chloride. Dispersoid particles were then suspended, in a dilute basic solution of the gold chloride, by stirring. Hydrazine, a reducing agent, was then added dropwise to the stirred gold chloride and thoria. The gold precipitated out and uniformly coated the oxide particles, producing alloys of good dispersoid homogeneity (fig. 2).

When the reduction process was complete the powdered alloy was filtered and vacuum-dried. The alloy powders were then degassed in a dry hydrogen furnace at 900° C for 4 h. This operation was needed to prevent blistering in the final wrought product. The powders were then pressed into 2.5-cm diameter slugs, canned in copper, evacuated, and extruded at 650° C with a 30:1 reduction in area. Fabrication parameters of individual alloys are shown in table I. Final fabrication of wire was done by cold-rolling with intermediate anneals.

3.3. Platinum Alloys

The platinum alloys were prepared by a process similar to that described above for the gold alloys. Chloroplatinic acid was made by dissolving platinum in aqua regia and then driving off the nitric acid by evaporation.

Dilute chloroplatinic acid and hydrazine were then added dropwise to a basic aqueous suspension of dispersoid particles heated to 75° C. When reduction was complete the mixture was filtered and vacuum dried. The platinum precipitated in this manner had a large active surface much like platinum black. Air-dried powders were pyrophoric.

The powders were prepared for fabrication by vacuum-outgassing at 800 to 1300° C for 1 h. The powders were then pressed into 2.5-cm diameter slugs, sintered, and placed in steel cans for extrusion. The platinum alloys containing 1.0 vol% ThO$_2$ and 1.8 vol% of ThO$_2$ were fabricated by sintering the loose powder at 1300° C and then extruding the gravity sintered slug. This procedure produced alloys which did not blister at temperatures below 1500° C. Three-metre lengths of 2.0-mm diameter wire were produced from these alloys by swaging. Extrusion was done at 1100 to 1300° C. Fabrication parameters are shown for individual alloys in table I. Fig. 3 shows a sample of a typical alloy produced by the above method; the homogeneity of the dispersoid is excellent.

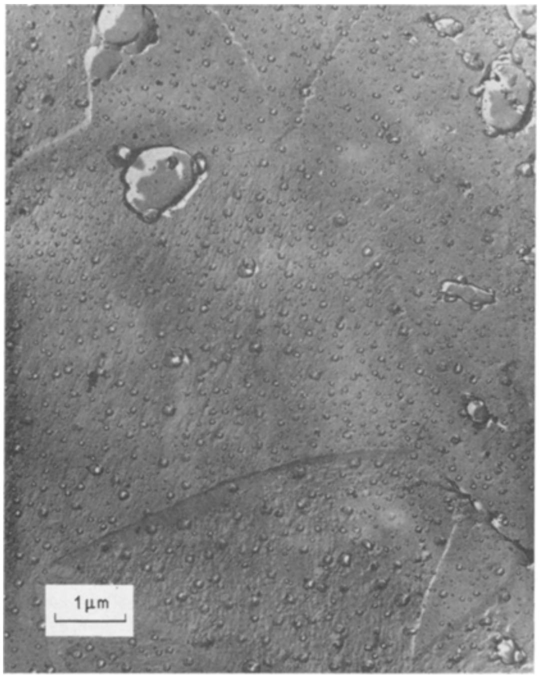

Figure 3 Electron micrograph Pt-6 vol% Al_2O_3 pressed and sintered at 1000° C for 30 min.

4. Results

The results of the tensile testing of the copper alloys are shown in table II and fig. 4. Samples of the dispersion-hardened wire were tested at elevated temperatures in an argon atmosphere. At 1000° C the 2.2 vol % ThO_2 alloy had a tensile strength of 16060 psi.

TABLE II Tensile properties of dispersion-strengthened copper alloys.

Condition	Ultimate tensile strength (psi)	0.2% yield strength (psi)	Elongation (%)
Cu-2.2 vol % ThO_2			
Cold-worked 50%	55000	52600	3.0
Annealing Temperature °C			
200—1 h	46000	41000	2.8
300—1 h	45200	44200	4.5
600—1 h	37400	18400	12
800—1 h	36300	22690	22.5
Elevated temperature tests in argon, °C			
200	42790		2.5
300	41420		3.0
600	33990		2.5
800	26220		2.5
1000	16060		2.0
Cu-5 vol % ThO_2			
Hot worked RT	43100	32100	1.0

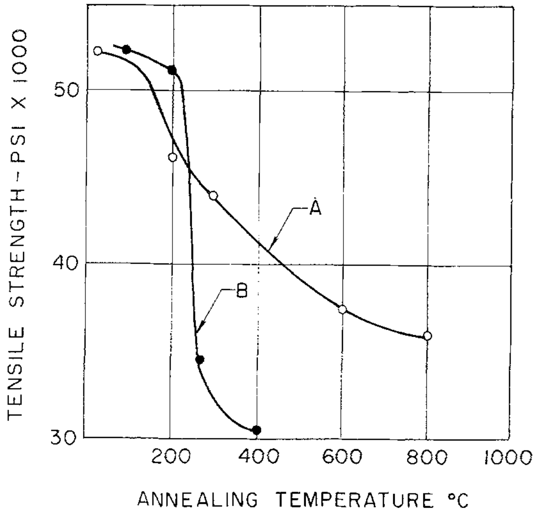

Figure 4 Tensile strength measured at room temperature for (*a*) Cu-2.2 vol% ThO_2 wire, 0.175 cm diameter, 50% cold-worked, after 60 min at annealing temperature shown, and (*b*) electrolytic tough pitch Cu, 70% cold-worked, after 30 min at temperature shown.

Recrystallisation characteristics were determined by annealing samples of the 2.2 vol % ThO_2 alloy at various temperatures and determining the Vickers hardness number. Complete recrystallisation does not occur until approximately 600° C. A Cu-5 vol % ThO_2 was cold-rolled and Vickers hardness readings were taken after annealing to determine recrystallisation (fig. 5).

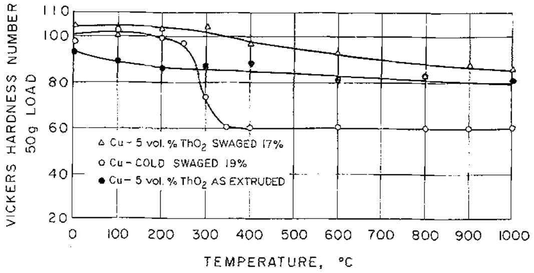

Figure 5 Vickers hardness curves for Cu and Cu-5.5 vol% ThO_2 heat treated 60 min at various temperatures shown.

The recrystallisation for the copper-5 vol % ThO_2 alloy is seen to be about 200° C higher than that of pure copper (fig. 5). An absence of grain-growth was observed in the dispersion-hardened

TABLE III Tensile properties of dispersion strengthened gold alloys.

Alloy	Test temperature (°C)	Ultimate tensile strength (psi)	Yield strength (psi) (0.2% offset)	Elongation
Au-3.4 vol % ThO_2				
Cold rolled 55%	25	31500	26500	2.7
	260	28500	25500	2.7
	537	17900	16300	2.0
Au-3.5 vol % Al_2O_3				
Cold rolled 60%	25	35000	32000	1.4
	260	32800	29500	3.2
	537	11100	8900	5.1
Au-6.4 vol % Al_2O_3				
Cold rolled 50%	25	35000	33000	1.0
	260	21900	19800	1.0
	537	8400	7100	2.1
Au made by powder metallurgy				
Cold rolled 60%	25	29700	26800	1.9
	260	16100	—	4.2
	537	7800	6900	12.0

alloys heated at temperatures up to 1000° C for 40 h.

The tensile properties of the gold alloys tested are summarised in table III. The best properties were shown by a 3.4 vol % ThO_2 alloy. Alumina showed considerable particle growth when heated at 900° C. After 40 h at this temperature the particle size had increased by a factor of three. Thoria containing alloys, under identical conditions, showed no detectable growth of the thoria particles. Specimens of gold wire made from gold powders containing no dispersoid prepared by the precipitation technique were also fabricated and tested for comparison purposes (table III).

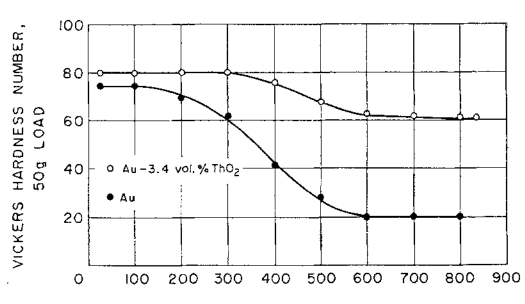

Figure 6 Vickers hardness curves for Au 3.4 vol %ThO_2 and Au made by powder metallurgy.

Recrystallisation curves based on Vickers hardness measurements of Au and Au-3.4 vol % ThO_2 alloy are shown in fig. 6. Recrystallisation in the Au-3.4 vol % ThO_2 alloy is seen to be some 200° C higher than in gold. No appreciable grain growth is noted in the dispersion-hardened alloy after annealing at 1000° C for 4 h.

The tensile properties of the platinum alloys are summarised in table IV and fig. 7. The 1.0 vol % ThO_2 alloy was degassed at 1000° C. This alloy was fabricated into 6 m of 0.175 cm diameter wire. The dispersoid particles showed little particle growth when heated at 1000° C. However, strength reduction due to outgassing was observed at 1100° C (table IV).

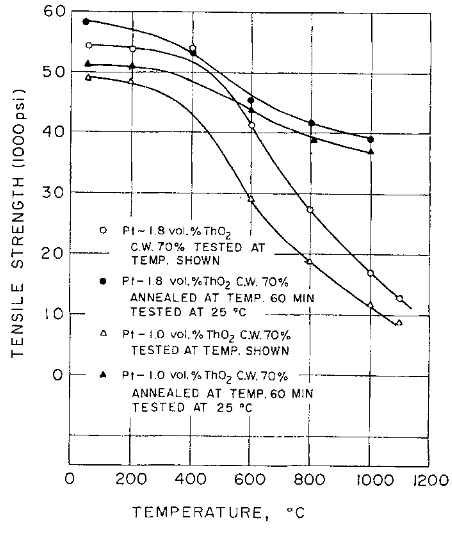

Figure 7 Tensile strength of Pt-ThO_2 alloys at various temperatures and at 25° C after annealing for 60 min at temperatures shown.

TABLE IV Tensile properties of dispersion-strengthened platinum alloys.

Alloy	Test temperature °C	Ultimate tensile strength (psi)	0.2% yield strength (psi)	Elongation %
Pt-1.8 vol % Al_2O_3				
Cold-rolled 50%	25	48000	47900	1.2
	260	37000	36500	1.5
	537	34900	33900	2.5
Cold-rolled + annealed at 1000° C	25	26500	18400	12.0
As extruded	25	36000	32000	11.0
Pt-2.2 vol % ThO_2				
Cold-rolled 60%	25	47900	47000	2.0
	260	42100	42000	2.0
	537	34500	33000	2.9
Cold-rolled + annealed at 1000° C	25	30300	14000	20.0
As extruded	25	37000	31500	10.0
Pt-1.0 vol % ThO_2				
Cold swaged 70%	25	49640	43309	2.5
	200	47700	—	3.0
	600	29167	—	3.5
	800	19220	—	2.5
	1000	12380	—	1.8
	1100	9535	—	2.5
Annealed 1 h at				
200	25	53150	—	2.0
600	25	44360	—	4.0
800	25	38930	—	5.0
1000	25	36800	—	6.0
Pt-1.8 vol % ThO_2				
Cold swaged 70%	25	54 226	—	2.8
	200	53 249	—	2.8
	400	53 528	—	2.8
	600	40 730	—	2.8
	800	27 438	—	6.6
	1000	16 970	—	8.8
	1100	13 227	—	13.0
Annealed 1 h at				
200	25	59 705	—	3.0
400	25	54 390	—	3.8
600	25	46 341	—	5.0
800	25	42 927	—	9.0
1000	25	39 512	—	12.0

The Pt-1.8 vol % ThO_2 alloy was made by degassing the powder at 1000° C and then extruding and swaging the sintered mass. This treatment eliminated the problem of outgassing but caused particle growth. After heating the cold-swaged alloy to 1000° C for 2 h there was some grain growth, but the grain size was still less than 3 μm in diameter. The oxide particles grew to about 0.1 to 0.3 μm diameter, but are still effective in increasing strength and retarding grain growth.

The resistivity of the various conductors was measured using a standard four-leads potentiometric method with a Leeds-Northrup K3 Potentiometer.

The resistivity as a function of temperature for the cold-worked Cu-2.2 vol % ThO_2 alloy are

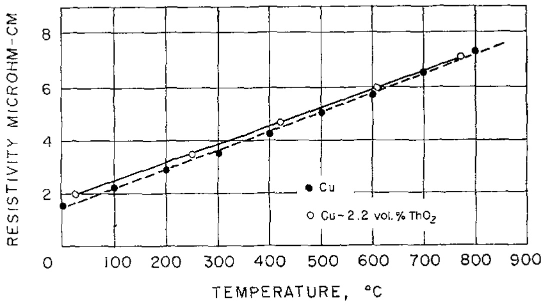

Figure 8 Resistivity versus temperature for Cu-2.2 vol % ThO_2 alloys and Cu.

shown in fig. 8 and compared to that of annealed Cu.

The resistivity as a function of temperature of dispersion-strengthened gold and platinum alloys are presented in figs. 9 and 10, respectively.

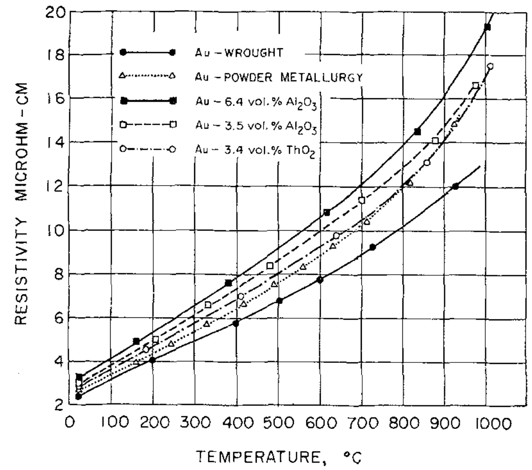

Figure 9 Resistivity versus temperature for Au—ThO_2, Au—Al_2O_3 alloys and Au.

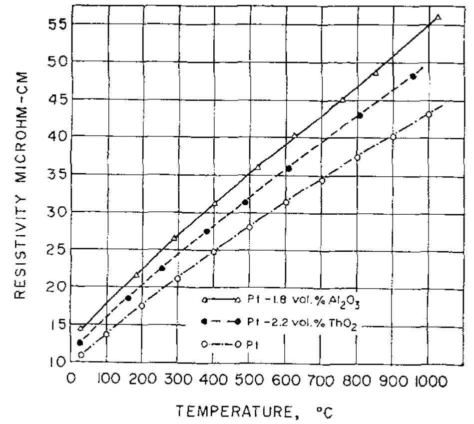

Figure 10 Resistivity versus temperature for Pt-2.2 vol % ThO_2, Pt-1.8 vol % Al_2O_3 alloys and Pt (wrought).

5. Discussion and Conclusions

Dispersion-strengthening of Cu, Pt and Au by the chemical plating technique produced alloys with a good homogeneous distribution of dispersoid (figs. 1 to 3). Thoria dispersoid particles 0.05 μm in diameter showed little or no growth up to 1000° C, in contrast to alumina particles which showed rapid growth.

In all instances the mechanical properties were superior to those of the elemental metals, especially at elevated temperatures. Optimum tensile strength and ductility were observed in alloys containing 1 to 2.5 vol % dispersoid. High dispersion-content decreased the ductility, making the alloys difficult to manipulate owing to the microcracking during swaging (table II). Figs. 4 and 7 and tables II to IV illustrate the high tensile strength achieved with increasing temperature after annealing treatments for Cu, Pt and Au alloys. A theoretical estimate of yield stress from equation 1 gives about half the observed value at room temperature for copper. This very approximate agreement with the Orowan theory improves when allowance is made for the polycrystalline nature of the specimen.

Hardness measurements (figs. 5 and 6) show that the alloying provides useful improvements in hot hardness and retards grain growth and recrystallisation.

In all instances electrical resistivity of the Cu, Pt and Au alloys was greater than that predicted by a simple volume effect due to the dispersoid. This is attributed to impurities and work-hardening introduced during the processing steps of plating, extrusion, rolling or swaging, rather than surface scattering of electrons on dispersoid particles for the reasons previously discussed in connection with equations 2 to 4. The slightly lower temperature coefficient of resistivity observed for Cu-2.2 vol % ThO_2 as compared with copper (fig. 8) may be attributed to the tendency for ThO_2 to absorb impurities at high temperatures. Similar behaviour is observed in Au-3.4 vol % ThO_2 alloys (fig. 9), but not in Pt-ThO_2 alloys (fig. 10). In all instances, Al_2O_3 dispersions produce a greater increase in resistivity for a given volume than ThO_2. This may be related to the lower free energy of formation for Al_2O_3, leading to a higher concentration of Al in the Au or Pt. matrix.

Alloys of Cu, Pt and Au plus 2 vol % ThO_2 can be recommended for applications requiring good tensile properties and/or hardness, combined with low resistivity and oxidation resistance (Pt, Au) at high temperatures. These alloys can be used at 1000, 1000 and 550° C, with a tensile strength of 17,000 psi (kg mm^{-}) and resistivities of 8.4, 50.0 and 8.3 microhm-cm respectively and can be fabricated into wire form.

Advances in the quantitative understanding of the mechanical and electrical properties of fine dispersions in metals require dispersion-hardened single crystal specimens. It is possible that these can be produced by strain-anneal techniques or alternatively by electron-beam zone-melting if gravity-induced segregation and clumping of the dispersoid phase can be avoided. If such specimens can be made, studies of electron and phonon scattering at low temperatures on small 200 to 500 Å particles would be of interest.

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