

THE CHANGE IN COLOUR OF A SILVER-GOLD ALLOY ON PLASTIC DEFORMATION

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Summary

The colour change when deformed samples of the alloy AgAu are annealed has been confirmed and an attempt has been made to measure it in terms of the movement of the spectral absorption edge. It is found that on annealing the absorption edge of a heavily deformed sample moves about $5 \pm 4 \text{ m}\mu$ toward shorter wavelengths. No such effect was observed in the pure metals, silver and gold. It is suggested that the effect may be connected with the presence of short-range order and/or with a migration of silver atoms to the surface in the annealing process.

I. INTRODUCTION

Marked colour changes on cold working alloys of silver and gold were noticed by Tammann (1919) (see also Tammann and Wilson 1928). He reported that whitish-green alloys in the range 60–70 wt. % Au became yellowish on heavy cold rolling and that the effect is more pronounced with some ternary alloys of silver, gold, and copper, the colour change increasing with increasing deformation. Lipson, Burstein, and Smith (1955) have observed a shift towards longer wavelengths of the spectral absorption edge of germanium when deformed. Boas (1957) has drawn attention to the influence of the Fermi energy on the position of the absorption band which might be expected to change on plastic deformation, thus resulting in a colour change when the absorption band is in the visible spectral region. Schulz and Tangherlini (1954) have noted the effect of annealing on the reflectivity of silver, gold, and other metals deposited on glass substrates. They report that a fresh deposit of gold was slightly orange in appearance, but after an annealing treatment this changed to the typical yellow of pure gold. The optical properties of evaporated films are anomalous and the effect noted by Schulz and Tangherlini is more likely to be connected with the method of deposition of the metal rather than a change in colour with deformation. Margenau (1929) reported a shift of the trough in the reflectivity curve of silver when samples were polished to varying degrees.

It is now known that the ternary alloys mentioned by Tammann consist of two phases and that they are subject to age hardening (McMullin and Norton 1949). The change in colour on deformation might be associated with phase separation rather than with energy stored in the deformation. It was decided, therefore, to examine the effect in the single-phase binary alloy of silver and gold.

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II. EXPERIMENTAL PROCEDURE

The range in composition mentioned by Tammann covers the equi-atomic alloy AgAu. An ingot was prepared and, after homogenization, the chemical composition was 65.84 wt.% Au or 51.36 at.% Au. The clean ingot was carefully rolled between clean smooth rollers until a strip about $16\frac{1}{2}$ in. long, 1 in. wide, and 0.03 in. thick was obtained, from which 14 specimens each about 1 in. square, were cut. This represented a deformation of the ingot by more than 90%. Seven of these, chosen alternately along the strip, were sealed under a nitrogen atmosphere and annealed for about half an hour at 400°C. Visual examination of all the samples showed that the annealed samples appeared whiter (or less yellow) than the untreated samples. This was confirmed by a number of independent observers.

Preliminary observations of the spectral reflectivity of all the samples showed marked but not spectacular differences between the annealed and deformed samples. Surface scratches, however, produced variations between otherwise similar samples. While these variations did not appear to vitiate deductions concerning the change in the absorption edge with deformation, nevertheless the variations so affected the reflectivity that analysis of the spectral reflectivity curves was rendered difficult. A scratched surface caused a reduction in the reflectivity compared with a less damaged one, particularly at the red end of the spectrum.

In order to confirm these preliminary observations and to obtain reliable numerical values for the movement in the absorption edge, samples were very carefully prepared from the original specimens. Attempts were made to prepare samples with similar surface finishes and one of each pair was annealed, the other remaining deformed. The deformation consisted of a reduction in thickness at least 90% in extent. For example, one pair had hand-polished surfaces; another pair was compressed between highly polished steel plates; another sample was compressed, cut into four pieces and two pieces annealed; another specimen was cut into half, each half rolled to the original size and one portion annealed. Several samples were re-rolled between highly polished steel rollers. No oil was used, the only lubricant being petroleum ether used as a grease solvent. In one case the spectral reflectivity of a deformed sample was measured before and after annealing; conversely, an annealed sample was examined spectrally, a piece was cut off and rolled, causing 80% reduction in thickness, and this deformed portion was examined. Some of the samples were annealed in a stream of hydrogen and others in a continuous vacuum, the annealing being carried out at 500°C for 1 hr.

The samples were handled with great care to avoid damage to the surfaces. Except in the case of the hand-polished samples, the surface of no specimen was touched by hand during or after the deformation process. They were mounted in 2 by 2 in. card holders as used for mounting film transparencies. The holders had been painted mat black to prevent reflection of light from the holder. Tests on samples having identical treatment showed that the Vickers hardness of the deformed samples was 130 ± 4 and that of the annealed samples, 50 ± 2 .

The spectral reflectivity measurements were made on a Beckman DK-2 spectrophotometer fitted with a reflection attachment consisting of an integrating

sphere. A magnesium oxide surface was used as a reference. The spectral reflectivity curve obtained gives the reflectivity of the sample, relative to that of magnesium oxide, plotted against wavelength. Checks were frequently made by comparing one sample against another, i.e. by using a deformed specimen as sample and an annealed one as reference. The slit width of the monochromator varied with wavelength, but, in the range 400–550 $m\mu$ the spectral band width ($2 \times$ half-intensity band width) was not more than 0.8 $m\mu$. In order to standardize the technique, all samples were placed against the aperture in the integrating sphere in the same way.

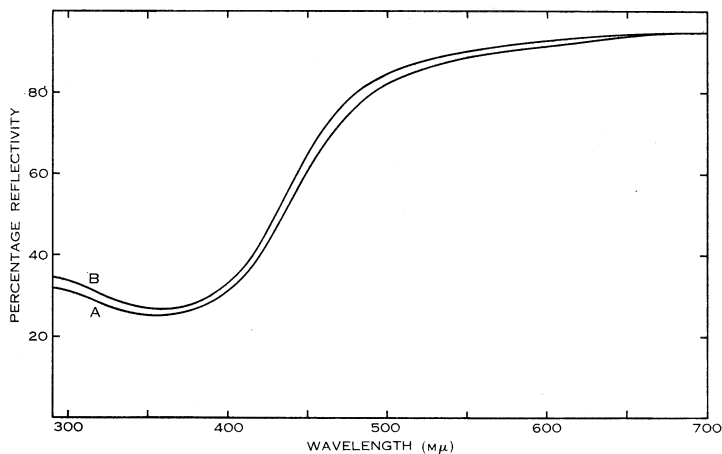


Fig. 1.—Spectral reflectivity curves of a silver-gold alloy as recorded on a Beckman DK-2 spectrophotometer (MgO as reference). Curve *A*: sample No. 7(a), deformed; curve *B*: sample No. 6, annealed.

They were tilted so that the reflected light beam was directed downwards below the horizontal plane of the entrance ports and an image of the monochromator slit formed on the lower half of the sphere. The angle of incidence was about 10° . To obtain good and consistent reflectivity curves it was found necessary to prepare samples as flat as possible. This was achieved by careful rolling, or by compressing, until the samples were between 0.5 and 0.8 mm thick. Thinner samples tended to warp and cause such divergence of the reflected light beam that light escaped through the entrance ports of the integrating sphere.

A pair of typical spectral reflectivity curves is shown in Figure 1. The shapes of the curves for annealed and deformed samples showed no significant difference in the ultraviolet but clear differences occurred in the slopes of the absorption edges between 400 and 500 $m\mu$. Thus measurements were not made at wavelengths less than 350 $m\mu$.

III. ANALYSIS OF THE CURVES

In order to compare the curves quantitatively they were examined in pairs, one curve each for a deformed and an annealed sample, or for the same sample

before and after annealing. Differences in reflectivity, spectral position, and slope of the absorption edge were determined.

To allow for differences in reflectivity at the red end of the spectrum the reflectivity at $600\text{ m}\mu$ of all specimens was assumed to be 100%, and the curves scaled accordingly. When this was done it was found that the reflectivity of the deformed samples for $\lambda < 600\text{ m}\mu$ was always less than that of the annealed samples, the difference being about 2% at $500\text{ m}\mu$, 4% at $450\text{ m}\mu$, 2% at $400\text{ m}\mu$, relative to 100% at $600\text{ m}\mu$. The maximum difference was about 5% at $435 \pm 5\text{ m}\mu$.

Numerical values for the shift in the absorption edge were obtained from each curve as follows. A tangent was drawn at the point of maximum slope and a chord was drawn through the curve at 550 and $650\text{ m}\mu$. Let these lines intersect at the point A . This point was found to be at $478 \pm 2\text{ m}\mu$ for annealed samples and at $484 \pm 2\text{ m}\mu$ for deformed samples.

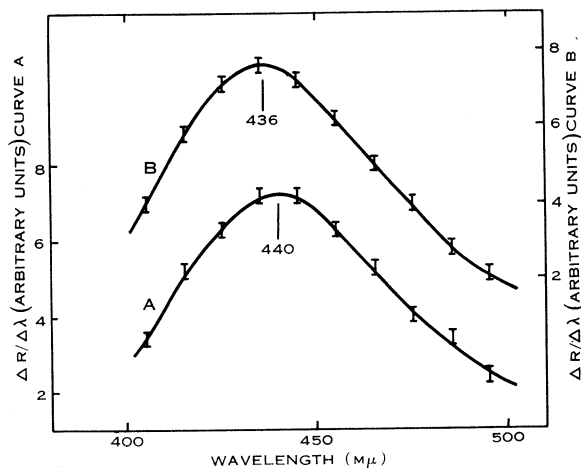


Fig. 2.—Curves showing $\Delta R/\Delta\lambda$ as a function of λ for a silver-gold alloy. Curve A: sample No. 7(a), deformed; curve B: sample No. 6, annealed.

The slope of the tangent at the point of maximum slope for annealed samples was 0.72 ± 0.04 (percentage reflectivity per $\text{m}\mu$) and for deformed samples was 0.67 ± 0.03 .

The rate of change of reflectivity with wave length ($\Delta R/\Delta\lambda$) was calculated by reading directly from the curves over the range 400 – $500\text{ m}\mu$. Curves of $\Delta R/\Delta\lambda$ versus λ were plotted and the maximum noted (Fig. 2). This maximum occurred at $435 \pm 2\text{ m}\mu$ for annealed samples and at $440 \pm 2\text{ m}\mu$ for deformed samples.

Details of the analysis are given in Table 1. The measurements for the hand-polished surfaces are included for comparison but the mean values given do not include these measurements. Even in this case, the change in wavelength with deformation is of the same order of magnitude as for untouched surfaces.

One pair of samples was examined on a Hardy spectrophotometer. Similar results were obtained with these samples as with samples on the Beckman instrument.

TABLE 1
ANALYSES OF REFLECTIVITY CURVES FOR SILVER-GOLD ALLOY

Mechanical Treatment of Sample	Deformed Samples				Annealed Samples			
	Sample Number	Wavelength at Point A ($m\mu$)	Slope $\Delta R/\Delta\lambda$ ($m\mu^{-1}$)	Wavelength at Point of Inflection ($m\mu$)	Sample Number	Wavelength at Point A ($m\mu$)	Slope $\Delta R/\Delta\lambda$ ($m\mu^{-1}$)	Wavelength at Point of Inflection ($m\mu$)
Rolled and hand polished	3	496	0.58	445	2	491	0.64	438
Compressed	7(a)	483	0.64	443	7(b)	476	0.71	435
	7(a)	484	0.73	440	7(a) 4 6	477 480 480	0.78 0.76 0.76	435 436 436
Rolled	11	482	0.64	440	10	476	0.66	438
	11	485	0.66	441	10	478	0.71	433
	11	486	0.69	435	14	480	0.70	430
Rolled and cross-rolled	15	482	0.68	439	14	477	0.69	433
	15	485	0.65	440	14	479	0.71	436
	15	486	0.67	439				
Rolled, cut, and rerolled*	15(a)	486	0.68	440	15(b)	480	0.73	436
Mean values (except hand polished)		484 \pm 2	0.67 \pm 0.03	440 \pm 2		478 \pm 2	0.72 \pm 0.04	435 \pm 2

* Pair examined on Hardy spectrophotometer.

It is seen that the absorption edge can be said to move $5 \pm 4 \text{ m}\mu$ towards the longer wavelengths when an annealed sample of an equi-atomic alloy of silver and gold is heavily deformed. The early observation of Tammann is thus confirmed and a quantitative estimate of its magnitude has been obtained.

IV. DISCUSSION

It might be argued that the movement in the absorption edge due to annealing a deformed sample was due to surface contamination occurring in the annealing process. This is not considered a likely factor for the following reasons: (i) different techniques of annealing did not affect the results; (ii) a deformed sample was examined before and after annealing, and an annealed sample was examined before and after rolling, giving the same shift of the absorption edge; (iii) electron diffraction examination of similar surfaces showed the presence of silver chloride on both types of sample but electron microscopic examination of replicas showed no noticeable difference in the surfaces and no general contamination. It is believed that any surface contamination would be transparent in the region 400–500 $\text{m}\mu$ and just as likely to be present on both types of sample.

Roughness on the surface of a metal will result in greater absorption due to multiple reflections; this was confirmed by deliberate roughening of a pair of samples. However, roughness on the surface did not influence the results, since it was noted that before "scaling" some rolled samples had greater and some less reflectivity at 600 $\text{m}\mu$ than annealed samples. The highly polished steel surfaces used in the deformation processes were successful in producing very smooth surfaces on the alloy samples. Furthermore, the samples were placed over the appropriate aperture of the integrating sphere in a number of different orientations. Very little variation was observed and such variations did not affect the position of the absorption edge. When scaled to 100% at 600 $\text{m}\mu$ the differences between the reflectivities at 440 $\text{m}\mu$ were still measurable whether the surface of the sample was highly polished or not. Though surface roughness can affect the absolute reflectivity, it is difficult to see why it should have a spectrally selective effect over the comparatively narrow range from 400 to 500 $\text{m}\mu$.

If the explanation of the shift in the absorption edge is to be found in terms of the effect of dislocations on the Fermi surface, then it follows that a similar shift should be obtained with pure metals such as silver and gold. In order to confirm the observations of Margenau on silver and Schulz and Tangherlini on gold, and to test the hypothesis that the absorption edge is affected by deformation, samples of silver and gold were prepared in the same way as for the alloy described above. The spectral reflectivities of a considerable number of samples were examined but no positive result was obtained. In the case of silver, the very steep absorption edge for deformed samples was within $+1 \text{ m}\mu$ of that for annealed samples. As the uncertainty was about the same order of magnitude, it is felt that the effect with silver, if any, was too small to be measured with the apparatus available. In the case of gold no shift in the absorption edge was observable. A decrease of about 3% in the reflectivity of annealed samples compared with deformed samples was observed between 470 and 480 $\text{m}\mu$. If this effect is real it is in the opposite direction from

that for the alloy. Finally, the colour change in the ternary alloy is in the opposite direction from that of the binary alloy. The annealed samples of the ternary alloy appear redder than the deformed samples. The explanation of the colour changes which occur on annealing of deformed samples must take these variable results into account.

It is possible to suggest two explanations of the colour change on annealing a deformed sample of the silver-gold alloy. It is known that the alloy shows a degree of short-range order. Norman and Warren (1951) estimated that, at temperatures below 300°C, the measured order was 24% of the way from disorder to perfect order. There is no evidence of long-range order in this alloy. The ordering process will modify the Fermi energy and hence influence the position of the absorption band. In order to account for the observed wavelength change of 5 m μ at 440 m μ a change of approximately 30 meV is required.

Alternatively it may be suggested that the silver atoms migrate to the surface during annealing. Such a migration could take place because of the relatively high diffusion rate of silver in the silver-gold alloy, and on the assumption that the surface energy of silver is less than that of gold. There was some microscopic evidence of surface migration but no evidence of a differential migration of silver with respect to gold.

It is possible to devise experiments to test both of the above "explanations", but such experiments would have unduly prolonged the research, which was undertaken simply to verify Tammann's early observation and, if possible, to attach a numerical magnitude to it.

V. ACKNOWLEDGMENTS

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VI. REFERENCES

- BOAS, W. (1957).—"Dislocations and Mechanical Properties of Crystals." p. 406. (Wiley: New York.)
- LIPSON, H. G., BURSTEIN, E., and SMITH, P. L. (1955).—*Phys. Rev.* **99**: 444.
- McMULLIN, J. G., and NORTON, J. T. (1949).—*Trans. A.I.M.E. J. Metals* **1**: 46, 858.
- MARGENAU, H. (1929).—*Phys. Rev.* **33**: 1035.
- NORMAN, N., and WARREN, B. E. (1951).—*J. Appl. Phys.* **22**: 483.
- SCHULZ, L. G., and TANGHERLINI, F. R. (1954).—*J. Opt. Soc. Amer.* **44**: 362.
- TAMMANN, G. (1919).—*Z. anorg. Chem.* **107**: 1.
- TAMMANN, G., and WILSON, C. (1928).—*Z. anorg. Chem.* **173**: 156.