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Solid Metal Embrittlement of Ti-6Al-6V-2Sn by Cadmium, Silver and Gold

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SOLID METAL EMBRITTLEMENT OF Ti-6Al-6V-2Sn
BY CADMIUM, SILVER, AND GOLD

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Abstract

Solid metal embrittlement of Ti-6Al-6V-2Sn has been observed with Cd, Ag, and Au. A threshold temperature of 477-505 K exists for Ag and Au, below which no embrittlement was observed. Embrittlement by Cd at 421 K was confirmed. No embrittlement due to Cu or Ni was observed at temperatures as high as 560 K. Scanning Auger analysis of Ag and Cd embrittled samples indicated that (1) the fracture path is intergranular, (2) surface diffusion is the limiting transport mechanism, and (3) surface diffusion of Cd and Ag is over the titanium oxide. The fracture process is discussed in relation to liquid metal embrittlement.

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Solid Metal Embrittlement of Ti-6Al-6V-2Sn
by Cadmium, Silver and Gold

R. E. Stoltz and R. H. Stulen

Solid metal embrittlement (SME) is defined as cracking of a stressed sample when held in contact with a solid metal species. Previous investigations (1,2) have shown that Cd can embrittle Ti-6Al-4V, Ti-8Al-1Mo-1V and Ti-3Al-13V-11Cr alloys at temperatures as low as 421 K (148°C). Earliest evidence of the effect of Ag on titanium alloys occurred in the failure of a Ti-alloy compressor wheel at high temperatures in the presence of silver chloride (3). Subsequent laboratory tests confirmed the effect of silver above 644 K (371°C) (3); however, only a single observation has been made of lower temperature embrittlement by silver (1). The present work more fully investigates the role of silver and is the first to report that gold is a solid metal embrittling agent for Ti-6Al-6V-2Sn (Ti-662). This study is also the first to use scanning Auger microscopy to analyse SME fracture phenomenon.

Experimental

All tests were performed on a 3.1 mm (.125 in) sheet of mill annealed Ti-662 with a composition given in Table I. The sheet was given a duplex annealing treatment of 1173 K (900°C)/2 hr + 1063 K (790°C)/2 hr with a resulting yield strength of 1014 MPa (147 ksi). An optical micrograph of the heat treated material is given in Figure 1.

Embrittlement tests were performed using the method employed by Meyn(2). Foils of the embrittling agent were press-fitted onto dogbone shaped flat specimens of Ti-662 using softened tool steel dowel pins. The samples had a minimum cross-section of 9.5 x 3.1 mm (.375 x .125 in). In order to

TABLE I

Composition of Ti-6Al-6V-2Sn sheet, wt %

<u>Al</u>	<u>V</u>	<u>Sn</u>	<u>Cu</u>	<u>C</u>	<u>Fe</u>	<u>N</u>	<u>O</u>	<u>Ti</u>
5.3	5.3	1.9	0.45	0.022	0.48	0.012	0.194	BAL

Figure 1. Microstructure of Ti-662 mill annealed plus duplex annealed.

The structure is composed of equiaxed primary α grains and transformed β (a mixture of α + β platelets).

achieve good physical contact between the Ti surface and the metal foils, sufficient clamping force was applied to generate a region of plastic deformation on the titanium sample. Samples were then dead weight loaded in a creep frame to a stress of 759 MPa (110 ksi), with the clamping force retained on the specimen throughout the test. The embrittling effect of each metal foil on the Ti alloy was studied as a function of temperature and hold time. After each test the samples were cooled to ambient and examined for surface cracking. Subsequently, specimens were broken open in 3-point bending to reveal the depth of crack growth that occurred during dead weight loading.

Results

Embrittlement results are summarized in Table II. Temperatures were varied from 560 K (287°C) to 421 K (148°C) for times of from 50 to 400 hours. Each test was performed twice. In order to prove out the experimental technique a test with Cd was performed at 421 K for 50 hrs. As has been reported for other titanium alloys (1,2) extensive intergranular cracking occurred. In the case of Ag and Au, an apparent threshold of from 477-505 K exists, below which no cracking was observed. Cu and Ni did not cause embrittlement up to 560 K, nor did the bare tool steel dowel pin in contact with the Ti-662 surface.

No systematic evaluation of crack depth versus time and temperature was attempted. However, at 505 K for 50 hrs. cracking with Ag extended to 250 μm (.010 in) while with Au the depth was only 50 μm (.002 in). In the Cd sample at 421 K for 50 hrs. the crack depth was $\approx$ 500 μm (.020 in). This difference suggests that the elements can be qualitatively ranked in their embrittling power Cd: Ag: Au.

TABLE II

Solid-metal Embrittlement vs Temperature and Time

<u>Embrittling species</u>	<u>Temperature</u>	<u>Time, hrs</u>	<u>Cracking Observed</u>
Ni	560 K (287°C)	50	No
Ni	560 K (287°C)	150	No
Cu	560 K (287°C)	50	No
Cu	560 K (287°C)	150	No
Ag	560 K (287°C)	150	Yes
Ag	505 K (232°C)	150	Yes
Ag	477 K (204°C)	150	No
Ag	449 K (176°C)	400	No
Ag	421 K (148°C)	400	No
Au	560 K (287°C)	150	Yes
Au	505 K (232°C)	150	Yes
Au	477 K (204°C)	150	Yes
Au	449 K (176°C)	400	No
Al	421 K (148°C)	400	No
Cd	421 K (148°C)	50	Yes

Scanning electron micrographs of the embrittled regions of the Cd, Ag, and Au tests are shown in Figure 2, a, b, and c respectively along with typical unembrittled regions from a test with Ni in Figure 2d. The brittle fracture mode is primarily intergranular with occasional evidence of cleavage through the α grains. Normal dimple rupture by void coalescence occurs in the absence of embrittlement (Figure 2d). Qualitatively, the amount of plastic tearing accompanying the intergranular fracture increases from Cd to Ag to Au.

Scanning Auger Microscopy (SAM) was performed to analyze the surface composition in the embrittled regions. Auger spectra were taken using a PHI model 545 SAM system with a nominal beam size of 3 microns. Other than simple de-greasing with acetone and ethyl alcohol, the air exposed sample fracture surfaces generated by the 3-point bending were untreated prior to Auger analysis. For each sample, numerous spectra were recorded for both the embrittled as well as non-embrittled regions.

Typical Auger spectra for the titanium alloy samples in contact with Cd and Ag are shown in Figures 3 and 4 respectively. A comparison of the spectra taken in the embrittled and non-embrittled areas shows very clearly the existence of Cd or Ag (Figures 3a and 4a) in the brittle fracture surface region. The presence of chlorine and silicon in Figure 3a and silicon in Figure 4a is attributed to handling of the specimen.

The enhancement of sulfur in the brittle regions was investigated in the following way. Samples of metallographically polished Ti-662 were argon ion sputter cleaned and heated at pressures $<10^{-9}$ torr. Approximately 0.8 monolayers of sulfur was observed after heating to 838 K (565°C) for 90 minutes.

Figure 2. Fracture surface of Ti-662 broken open in bending following exposure to solid (a) Cd, (b) Ag, (c) Au, (d) Ni. Embrittlement and intergranular fracture occurs with Cd, Ag, and Au, while no embrittlement and dimple rupture occurs with Ni.

Figure 3. Typical Auger spectra from Ti-662 fracture surfaces exposed to Cd; (a) intergranular brittle region (b) dimple rupture non-embrittled region. Beam parameters: $E_p = 10$ keV, $I_p \approx 1 \mu\text{A}$

Figure 4. Typical Auger spectra from Ti-662 fracture surface exposed to Ag; (a) intergranular brittle region, (b) dimple rupture non-embrittled region. Beam parameters: $E_p = 10$ kev, $I_p \approx 1\mu\text{a}$

Hondros and Seah(4) show that in general for a given material the observed trends in surface segregation can be correlated with grain boundary segregation. The enhancement of sulfur in the brittle intergranular regions, Figure 3a and 4a, is therefore interpreted as grain boundary segregation during heat treatment. The smaller sulfur peak in the ductile regions is due to the absence of intergranular facets.

In Figure 5, line scans illustrating the variation of the cadmium and silver signals are shown superimposed on SEM images generated for the identical regions. Here the Auger data is generated by scanning the electron beam in one dimension across the sample fracture surface with the electron analyzer set to an energy range corresponding to the element of interest; in this case Cd or Ag. The arrows in Figure 5 indicate the actual path of the electron beam. The dotted line separates the brittle and non-brittle regions.

In both Figures 5a and 5b the Auger signal falls to zero at the interface between the brittle and ductile fracture regions. The embrittling element exists only in regions exhibiting intergranular or cleavage cracking. The large variations in signal across the brittle zone are associated with topographic features of the surface and the orientation with respect to the Auger analyser.

Additional Auger analysis was performed on the fracture surfaces of titanium samples which had been tested while in contact with gold. Figure 2c shows an example of the brittle fracture surface region observed in these samples. No Auger signal corresponding to gold was detected for these samples. Using known Auger sensitivity factors for gold (5), we estimate the lowest detectable concentration for the surfaces under investigation to be approximately 1 atomic %. The inability to observe Au is likely due to carbon contamination of the embrittled surface.

Figure 5. Superposition of Auger scan profile for (a) Ag (351 eV) (b) Cd (316 eV) and the SEM images for the same regions. In both cases the arrow indicates the exact trace of the electron beam used to generate the surface composition profile (Cd test: 421 K/50 hrs, Ag test: 560 K/150 hrs). The dashed line indicates the boundary between brittle and non-brittle regions.

Upon completion of the analysis of fracture surface composition the Cd and Ag SME samples were sputtered with a 5 keV argon ion beam. The brittle regions were analyzed for Ti, O and either Cd or Ag and the results of concentration versus sputter time are given in Figure 6. A sputter time of 10 min. corresponds to approximately 640 Å. The actual sputter rate on the SME samples may, however, vary considerably due to the unknown sputter yields of this particular titanium alloy. In addition some uncertainty is introduced by surface roughness of the sample which varies the angle of the incident argon beam with respect to the surface normal at the analysis point of the Auger beam.

A number of points can be made from the data in Figure 6. In both Cd and Ag SME samples the embrittling species is only on the surface and not in the bulk alloy. In the Ag sample the concentration of silver drops to zero in a shorter time than that of oxygen. This indicates that silver is only on the top of the oxide and not dispersed through the oxide or at the oxide-metal interface. In the case of Cd, the cadmium signal drops to zero after 10 minutes indicating as well that Cd exists on top of the oxide. The interpretation of the apparent increase in Cd signal at times greater than 10 min. is complicated by the fact that Cd and lower energy Ti Auger lines overlap. It is likely that the increase is due to the emergence of these Ti lines, but the possibility of Cd dispersed through the oxide cannot be ruled out.

Discussion

Two recurrent questions in the analysis of solid metal embrittlement deal with the limiting transport mechanism and the physical action of the element at the crack tip. In a study of SME of steels, Lynn, et al, (6)

Figure 6. Sputter profiles of intergranular fracture surface region illustrating variation in primary oxide constituents as a function of sputter time; (a) Ag, (b) Cd (sputter rate is ≈ 64 Å/min).

suggest that due to the large variation in vapor pressures for elements that cause embrittlement, vapor phase transport is not the limiting transport mechanism. The results of Ag and Au tests confirm this conclusion. Table III gives the vapor pressure of Ag and Au at the lowest temperatures where embrittlement is observed, along with Cd at 421 K. Ideal gas calculations show that one monolayer is deposited per second at a vapor pressure of 10^{-6} torr (assuming a sticking coefficient of 1). Thus it would take an unrealistic $10^{13} - 10^{25}$ s for a monolayer of Ag or Au to deposit. Since the sputter data for Ag show no silver in the bulk alloy, surface diffusion is the only possible transport mechanism. In the case of Cd the vapor pressure is high enough so that at 421 K both vapor transport and surface diffusion could occur.

The existence of Ag and Cd primarily on top of the titanium oxide (Figure 6) suggests that surface diffusion from the source to the crack tip occurs over the titanium oxide. In order to sustain continued cracking, sufficient build up of embrittling species must occur at the crack tip. This build up is in dynamic competition with oxidation of the freshly exposed surface. These dual steps of diffusion and build up can explain the observation that cracking in Cd-Ti couples occurs in vacuum more readily than air (1). In vacuum more Cd can arrive at the crack tip before a thick oxide forms. Also, it is observed that Cd induced cracks are self limiting in depth (2). Though the stress intensity increases as the crack grows, the distance over which cadmium must move is longer and the flux arriving at the crack tip decreases. Since oxygen is transported in the vapor phase, the oxidation rate is not limited by crack length and thus, once the crack is long enough, the crack tip tends to oxidize before it is sufficiently embrittled to continue growing.

TABLE III

Vapor Pressure of Embrittling Elements

<u>Element</u>	<u>Temperature</u>	<u>Vapor Pressure log₁₀ torr</u>
Cd	421 K	-5.0
Ag	505 K	-19.5
Au	477 K	-31.6

These results indicate the need for measurements for surface diffusion over both clean titanium and titanium oxide and diffusion through the oxide. These experiments are underway.

The physical action of the embrittler at the crack tip remains an open question. Meyn (2) has suggested that solid metal embrittlement should follow the general tendencies of liquid metal embrittlement (LME), except for differences in transport. Westwood and Latanision (8) note that in a typical LME system the elements have little mutual solubility and little tendency for compound formation. Binary phase diagram data (9) shows that in the Ti-Cd, Ti-Ag, and Ti-Au systems stoichiometric compounds do form. In Ti-Au there is low mutual solubility though it appears that Ag is soluble in Ti up to 6%. Thus the guidelines suggested for LME do not hold for SME of Ti.

The unifying observation in both SME and LME is that the fracture is intergranular, indicating a reduction in the cohesive strength of the grain boundaries. Further experiments in pure polycrystalline metals are necessary. These experiments should be combined with calculations of how the interaction of foreign atoms with host grain boundaries reduces the cohesive strength.

Summary

1. Ti-6Al-6V-2Sn exhibits solid metal embrittlement in contact with Cd, Ag, and Au. No effect is observed with Ni or Cu.
2. A threshold of 477-505 K exists for Ag and Au, below which no embrittlement occurs at times up to 400 hours.
3. Surface diffusion is the limiting mode of transport to the crack tip. Auger analysis shows that Cd and Ag diffuse over the titanium oxide rather than over the base metal.

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