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~~APPENDIX VI~~

SOLID SOLUTION WEAKENING OF
B.C.C. SOLID SOLUTIONS

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SOLID SOLUTION WEAKENING OF B.C.C. SOLID SOLUTIONS*

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Introduction

Solid solutions of B.C.C. metals quite contrary to F.C.C. metals often produce solution weakening, in particular, dilute solid solutions. To be more specific about solution weakening, it is necessary to take into account the division of the yield stress into its two components; namely, the thermal component (called the effective stress), τ^* and the athermal component, τ_μ . The solute addition can affect both components of the flow stress; however, it usually increases the athermal component (as in the F.C.C. cases,) whereas it can increase or decrease the effective stress. The solution weakening mentioned only applies to a decrease in the effective stress due to the solute additions.

The initial observations of solid solution weakening, as noted by Arsenault (1) and Ravi and Gibala (2), were explained in terms of a scavenging mechanism. There are two factors which must be demonstrated to prove scavenging is the sole mechanism; one, the interstitials act as the short range barriers (i.e., a barrier that can be overcome by the thermal fluctuations) which oppose dislocation motion; and two, the substitutional solute addition acts as a scavenger of interstitials from random solid solution. It was first hypothesized by Weertman (3) and Armstrong (4) and discussed in greater detail later, by Arsenault (5) that solid solution weakening can be explained by another mechanism, namely, the reduction of the Peirls' stress (e.g. due to a reduction of modulus). Recently

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this explanation of solid solution weakening has been questioned, and the concept of scavenging again introduced.

An internal friction investigation was performed on three group V solid solutions which exhibited solution weakening in order to verify whether the correct mechanism was predicted from the mechanical property tests. These alloys were Ta + 2a/o W, Ta + 9.2 a/o Nb, and V with concentrations of Ti as high as 20 atomic percent. In order to make the interpretation of the results more straightforward a single interstitial, namely, oxygen was selected for this study. The results of this investigation will allow identification of which of the two mechanisms is operative in the three systems studied.

Experimental Techniques

Mechanical property investigations to determine the mechanism responsible for solution weakening in the Ta - Nb, Ta - W, and V - Ti alloy systems have been performed by Arsenault (5), Das and Arsenault (6), and Keith (7) and Pink and Arsenault (8) respectively. These investigations consisted of tension and compression tests on single and poly-crystalline samples as a function of temperature and strain rate. This type of tests yield the activation parameters as a function of stress and strain. These results can be utilized to determine if there is or is not a change in the Peierls' stress.

To determine if any of the solid solutions studied above exhibit scavenging, internal friction tests are required. Such tests were performed with a K² type inverted torsional pendulum

at frequencies in the 1 to 2 Hertz (Hz) range. Polycrystalline wire specimens of nominally 0.030 inch diameter by 2.5 inches long were prepared by cold swaging (in most cases, specimens from the tension and compression tests), and subsequent annealing at about 1000°C for one hour in a vacuum of less than 10^{-8} Torr to remove the cold work. Oxygen was added in incremental steps to these specimens along with high purity control specimens of V and Ta (which were utilized to determine the interstitial oxygen concentrations added to the alloy specimens) at oxygen partial pressures of nominally 10^{-6} Torr. After the oxidation treatment the specimens were annealed to homogenize the oxygen addition. Internal friction tests were then performed through the temperature range corresponding to the oxygen peak temperature in these alloys, and also at higher temperatures to insure the absence of carbon and nitrogen contamination during the oxidations. The incremental oxygen concentrations were determined from the maximum damping value of the control specimens utilizing relaxation strengths per atomic percent solute of Hasson and Arsenault (9) for oxygen in V and of Powers and Boyle (10) for oxygen in Ta.

Experimental Results

The internal friction results for the Ta + 2% W specimen with an initial oxygen content of 747 ppm atomic is presented in Fig. 1, where a significant damping peak is evident for the as received condition. Thus, it appears that the Ta + 2% W alloy does not show scavenging. An incremental addition of oxygen was made to this alloy and the oxygen peak increased (Fig.1). The ratio of the oxygen concentration increase in the alloy to oxygen concentration increase in the Ta control is defined as the "pick-up", and this ratio was 0.473 for the first addition and 0.603 for the second addition. The activation energies, as determined by half width analysis, were 15.8

14.4, and 15.9 Kcal/mole for the as received, first and second oxidations, respectively.

The internal friction results for the Ta+9.2% Nb alloy which had 93 ppm-atomic oxygen in the as received specimen are given in Fig. 2. The initial results for the as received specimen are somewhat suggestive of scavenging, because the damping peak is so small. After the first oxidation increment of 873 ppm-atomic, however, the peak became more definitive. thus, niobium does not act as a scavenger. The ratios of interstitial oxygen increase in the alloy to the Ta control were 0.763 and 0.717 for the first and second oxidations. The corresponding activation energies were 11.1 and 11.5 Kcal/mole with the as received value at 11.7. These activation energy values are about 40 percent lower than for the Ta + 2% W alloy.

The internal friction results for a V + 1.31% Ti alloy are given in Fig. 3. As can be seen in the Fig. 3, it takes oxygen concentrations in excess of 9000 ppm-atomic to produce a definite oxygen peak. Hence, Ti is denoted a scavenger. Instead of a broad peak which is representative of a substitutional atom which has a strong influence on interstitials, a double peak resulted. The high temperature peak is associated with the reaction of the Ti with the oxygen interstitial atoms. The peak temperature for the high temperature peak depends on concentration, and this result is somewhat indicative of a multiple relaxation process (i.e., just not an Ti - O reaction). A plot of the above results for Q^{-1} of the V - O peak against oxygen concentration shows that it takes about 1.5 Ti atoms to scavenge one oxygen atom. This result might indicate that the oxygen combines with the titanium to form stoichiometric $Ti_3 O_2$. Results from electron microprobe analyses show a

depletion of the titanium due to the anneal and oxidation treatments, and the Ti to oxygen ratio would then approach one.

Discussion

The three alloy systems studied represent combinations of the group V metals with group IV metals (e.g. the V - Ti alloy), with another group V metal (e.g. the Ta - Nb alloy), and with a group VI metal (e.g. the Ta - W alloy). The group IV metal Ti has been predicted to act as a scavenger of interstitials (11). Titanium has both a high affinity for oxygen and also a large solubility. The solubility of oxygen in Nb is relatively high, while there is almost no solubility of oxygen in W.

The scavenging action of titanium in vanadium is rather explicit in that the V - O peak normally associated with the presence of a random interstitial oxygen does not appear until the concentration of oxygen added to the alloy is equal to the substitutional solute concentration. When the substitutional solute concentration, x_s , is greater than the interstitial solute concentration x_i , the effect of interstitial atoms therefore on the effective stress could be considered negligible. Now for the case of $x_s > x_i$, where solution weakening is still found, the solution weakening can not be explained in terms of the scavenging mechanism. This case was found by Pink and Arsenault (8) for V + Ti alloys of concentrations to 20 w/o Ti. The solution weakening was explained by the reduction of the modulus of the alloy which reduces the Peierls' stress. Thus, in this alloy system which scavenging has been demonstrated

by internal friction tests, the mechanical property tests actually show the mechanism responsible for the solution weakening is the reduction in Peierls' stress mechanism. This is a significant result in that it shows the importance of performing both internal friction and mechanical property tests in order to determine the exact mechanism responsible for solution weakening in the B.C.C. solid solution.

The internal friction results for the tantalum solid solutions show somewhat different characteristics for the substitutional-interstitial interactions, but they do not show the presence of scavenging. The broadness of the Ta - Nb oxygen peak is reflected in its rather low activation energy of about 11 Kcal/mole (compared to 26 Kcal/mole of Powers and Doyle (10) for Ta - O) . The broadness is indicative of a strong influence of the substitutional atoms on the interstitial atoms as suggested by Gibala and Wert (12). This influence, however, does not affect the apparent solubility of the interstitial, as attested to by the high interstitial pickup ratio, but the interstitials behave differently in the neighborhood of the solute atoms than they would in a pure matrix of tantalum. The mechanical property results of Arsenault (6) have shown the operative mechanism responsible for solution weakening in this alloy to a reduction in the Peierls' stress. Hence the mechanical property results and the internal friction results do not conflict.

The tantalum + 2 at/o tungsten internal friction results on the other hand are more interesting. The pickup ratio for interstitial oxygen at the starting concentrations was abnormally low and the presence of tungsten may have some effect on the

solubility oxygen in the alloy. Since there is no appreciable solubility of oxygen in tungsten, the formation of some oxides at the low oxygen concentration might be expected. The activation energy for the Ta + 2 a/o W alloy was 40 percent higher than in the Ta + 9.2 a/o Nb case which also indicates that the presence of tungsten does not drastically effect the normal oxygen interstitial mobility in the tantalum matrix. Thus, tungsten, a group VI metal solute might be considered as intermediate in its influence on the random interstitials between titanium a group IV solute and niobium a group V solute. However, the main point is that tungsten does not act as a scavenger.

Conclusions

The internal friction results for V + Ti show scavenging of the interstitials by titanium occurs, however, the activation parameters derived for slip along with the fact that the weakening increases with increasing is due to the reduction in the Peirls' stress mechanism. The internal friction results indicate the scavenging action of titanium is due to a chemical attraction between the titanium and oxygen until the interstitial oxygen has reached the concentration of the substitutional addition. One important conclusion from the above results is that internal friction and mechanical property are required to identify the exact mechanism responsible for the solution weakening.

The tantalum solid solutions showed slightly different behaviors in that niobium is representative of an influence of the substitutional atoms on the interstitial atoms, while tungsten shows some characteristics of a pseudo-scavenger at

low interstitial concentration but very little effect on the normal Ta - O internal friction peak at moderate levels of interstitial concentration. The activation parameters of slip from mechanical property tests of these alloys showed the Peierls' mechanism was the operative mechanism responsible for solution weakening, and, thus, the internal friction results were in agreement with the conclusions from the mechanical property tests.

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FIG. 1: Internal friction vs. temperature for tantalum + 2% tungsten (background damping = 0.00055 ; $f = 1.15$ Hz)

FIG. 2: Internal friction vs. temperature for tantalum+9.2% niobium.
(background damping=0.00016; $f=2.32$ Hz)

FIG.3: Internal friction vs. temperature for vanadium+1.31% titanium SN 12B.
(background damping=0.00020; $f=1.72$ Hz)