THE SOLUBILITY OF OXYGEN IN TRANSITION METAL ALLOYS

R. T. BRYANT

Imperial Chemical Industries Limited, Research Department, Metals Division, Witton, Birmingham (Great Britain)

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SUMMARY

The solubility of oxygen in niobium and solid-solution alloys of niobium with other transition metals of Groups IVA, VIA, VIIA and VIIIA has been measured. The solubility of oxygen in niobium over the temperature range $700^{\circ}\text{C}-1550^{\circ}\text{C}$ obeys the relation: $--\log_e N = 8,600/RT + 0.516$ where N is the atomic fraction of oxygen in solution.

Additions of molybdenum, rhenium and ruthenium to niobium all reduce oxygen solubility, zero solubility being reached when the electron/atom ratio of the alloy is about 5.75. Additions of titanium increase the oxygen solubility, but zirconium, which forms a very stable oxide ZrO_2 , reduces oxygen solubility markedly.

It is concluded that the solubility of oxygen in transition metal alloys is largely electronic in nature, solubility being small if the electron/atom ratio of the alloy exceeds 5.75, and being very much larger in alloys of a lower electron/atom ratio, the oxygen dissolving with a positive charge.

INTRODUCTION

Oxygen is known to be readily soluble in transition metals of Groups IVA and VA of the Periodic Table and relatively insoluble in elements of Groups VIA, VIIA and VIIIA. For example, titanium (Group IVA) can dissolve up to about 33 at.% oxygen, niobium (Group VA) less than 10 at.% oxygen and molybdenum (Group VIA) almost none. Systematic variation in oxygen solubility from one Group to another, especially since niobium and molybdenum both have body-centred cubic structures with similar lattice parameters, suggests that oxygen solubility may be governed by electronic effects. The present work was designed to test this hypothesis by demonstrating the effect of addition elements of different valencies on the solubility of oxygen in a transition metal. Niobium was used as the base material. Alloving additions having appreciable solid solubility in niobium were chosen so that the electron/atom ratio could be changed without affecting the body-centred-cubic structure. Ideally these should all have come from the same Period of the Periodic Table, but as technetium was not available, rhenium was substituted. The metals used were zirconium, molybdenum, rhenium and ruthenium, representing Groups IVA, VIA, VIIA and VIIIA. Niobium-titanium-oxygen alloys were also investigated.

PREPARATION OF ALLOYS

Niobium used as starting material was in sheet form and contained the following impurities: 0.02% C, 0.03% O₂, 0.03% N₂ and 0.15% Ta.

For experiments on unalloyed niobium the starting material was purified by re-

sistance heating strips about 1/2 in. wide and 1/8 in. thick, at a pressure of less than 10^{-4} torr for a period of thirty minutes at a temperature just below the melting point. The purification brought about by this procedure is attributable to two effects, firstly the reaction of carbon with oxygen to form carbon monoxide which is removed by the pumps, and secondly the removal of oxygen and nitrogen by vaporization from the hot central portion followed by reabsorption of the gases at the cooler ends of the strip. The hardness of the resulting strip was about 40 DPN in the central region, compared with a hardness of 140 DPN for the starting material. Subsequent analysis for C and O₂ gave less than 0.01 wt.% of each of these elements.

Alloys of niobium with the above elements were prepared by arc melting in a small laboratory arc furnace, resulting alloys being in the form of buttons weighing about 7 g. Alloying additions in powder form, namely rhenium, ruthenium and the niobium pentoxide were pelletted before melting. Specimens to which metallic alloying additions had been made were homogenised after melting by heating *in vacuo* for one week at a temperature of $1450^{\circ}-1650^{\circ}C$.

EXPERIMENTAL METHODS

Oxygen absorption from an oxide film

This method of determining the solid solubility of oxygen in a metal or alloy relies on the establishment of equilibrium between an oxide film on the surface of the sample and a saturated solid solution of oxygen in the metal, solubility being measured by removing the oxide scale after equilibrium has been reached and analysing the underlying metal for oxygen. It is only applicable to pure metals or to alloys in which the oxides of the solute element are less stable than those of the solvent element. If the alloying additions form very stable oxides, internal oxidation occurs and renders the method useless.

Reaction between the specimen and a known amount of oxygen took place in an apparatus of the type shown in Fig. 1. Samples of known weight (about 0.2 g) were placed in a small bore silica tube, and heated under vacuum to remove any hydrogen present. The sample tube was then sealed off from the rest of the apparatus by closing tap A. Oxygen from the atmosphere was admitted to the sealed specimen tube by heating a silver tube (B) to about 800° C, at which temperature oxygen diffuses through silver quite readily. The total volume of the apparatus was known, and consequently



Fig. 1. Oxygen absorption apparatus.

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the amount of oxygen admitted could be determined by measuring the pressure in the system by means of a manometer filled with silicone oil of very low vapour pressure. Sufficient oxygen was admitted to exceed the estimated solid solubility limit of the specimen. In most cases the quantity of oxygen added was equivalent to about 0.8 wt.%. More than this, however, was required to saturate samples of pure niobium heated at temperatures above 1300°C. When sufficient oxygen had been admitted the silver tube was allowed to cool to room temperature so that no more oxygen could diffuse in or out of the apparatus. The sample was then heated to a temperature slightly lower than that at which it was desired to establish equilibrium, and allowed to absorb all the oxygen available, after which it was brought into equilibrium at the temperature at which solubility was to be determined. For temperatures up to 1000°C the specimen was heated in situ in the absorption apparatus. When the heat-treatment temperature lay between 1000°C and 1200°C the sample tube was sealed off by closing tap C, detached from the absorption apparatus and heated in a Kanthal wound resistance furnace. For heat-treatment at temperatures above 1200°C the sample was removed from the specimen tube altogether (care being taken not to disturb the oxide film) and heated at the desired temperature under vacuum by radiation from resistance heated tantalum strips.

The time required to establish equilibrium was determined by measuring specimen hardness after different heating times. Since oxygen hardens niobium appreciably, any change in oxygen content is accompanied by a change in hardness. It was therefore assumed that when no further hardness increase occurred, oxygen equilibrium had been established. For pure niobium twenty-four hours at 700° C were required, or four hours at 1000° C.

In order to prevent the precipitation of oxides from the saturated solutions on cooling, samples were cooled from the equilibrium temperature as quickly as possible. When heating had been carried out in the silica specimen tube, the tube itself was plunged into water; samples heated by radiation were quenched rapidly by a direct stream of water admitted from an exterior reservoir by opening a vacuum tap. No oxide precipitate which might have formed on cooling could be seen in the microstructure of any of the samples and it was therefore assumed that these cooling procedures were sufficiently rapid to prevent precipitation.

After quenching, any remaining surface oxide was removed by pickling in a mixture of five parts HNO_3 to one part HF, and the resulting samples were analysed for oxygen by means of vacuum fusion.

Metallographic method

Attempts to determine oxygen solubility in niobium-zirconium and niobium-titanium alloys by the above method failed due to the formation of an internal oxide precipitate. A standard metallographic technique was thus employed for these systems. Alloys were prepared by arc-melting alloy buttons with compacts of pure niobium pentoxide.

EXPERIMENTAL RESULTS

Pure niobium

Determination of solubility by oxygen absorption. The solubility of oxygen in pure niobium was determined over the temperature range 700°C-1550°C as described

above. Results are presented in Fig. 2 in the form of an Arrhenius plot, from which it can be deduced that the relationship:





where N = atomic fraction of oxygen in the saturated solution, R = the gas constant and T = the absolute temperature holds with a fair degree of accuracy. The heat of solution associated with the dissolution of oxygen from the oxide phase is therefore 8.6 kcal/g atom oxygen. The oxide phase existing in equilibrium with the solid solution was found by X-ray examination to be NbO¹.

Solubility of oxygen in alloys of niobium with elements of Groups VIA, VIIA and VIIIA

(a) Niobium-molybdenum alloys. Alloys containing up to 75 at.% Mo were studied. Results set out in Fig. 3 indicate that oxygen solubility falls with increasing molybdenum content reaching a value lower than that measurable by vacuum fusion at 75 at.% Mo. Solubility does not appear to fall in a uniform manner, an inflection being observed between 12 and 35 at.% Mo. Since the extent of oxygen solubility is governed partly by the properties of the oxide in equilibrium with the solid solution,



Fig. 3. Solubility of oxygen in niobium-molybdenum alloys at 1000°C.

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this departure from a smooth curve may be due to a change in the oxide formed as the molybdenum content is increased, but the possibility that it reflects some electronic change within the metal cannot be disregarded.

(b) Niobium-rhenium alloys. Niobium-rhenium alloys containing up to 30 at.% Re were investigated. Oxygen solubility results are presented in Fig. 4. Rhenium addi-



Fig. 4. Solubility of oxygen in niobium-rhenium alloys at 1000°C.



Fig. 5. Solubility of oxygen in niobium-ruthenium alloys at 1000°C.

tions reduce the solubility of oxygen in niobium, and by extrapolating the curve in Fig. 4 by 5 at.% Re it may be seen that oxygen solubility reaches a very low value at about 35 at.% Re. An initial small increase in oxygen solubility at about 3 at.% Re was observed, but this may be due to changes in the oxide in equilibrium with the metal.

(c) Niobium-ruthenium alloys. The composition range of the niobium-ruthenium alloys studied extended to 40 at.% Ru. The alloys, however, contained appreciable oxygen in the as-cast condition—0.047% oxygen in the niobium-30% ruthenium alloy—this being attributable to the presence of oxygen in the only available ruthenium starting material.

The results are presented in Fig. 5. Again, oxygen solubility falls rapidly with increasing ruthenium content, a solubility figure equal to the oxygen content of the as-cast button being reached at about 25 at.% Ru. Since in alloys having zero oxygen solubility any oxygen present in the starting material would be precipitated out in the form of internal oxide, and would be included in the analysis for dissolved oxygen carried out on the metal brought into equilibrium with the external oxide film, the apparent solubility of oxygen in the alloys as determined by the oxygen absorption method cannot fall below the level of the initial oxygen content of the alloys concerned. It is reasonable to conclude, therefore, that when the measured solubility reaches this figure the actual solubility is zero, and that in the present instance zero solubility occurs at about 25 at.% Ru. Support for this argument is given by the fact that signs of oxide precipitation were seen at the grain boundaries in the microstructure of the 30 at.% Ru alloys.

The value for 40 at.% Ru is suspect both because of original oxygen present in the cast button, and because this alloy showed traces of an intermetallic phase in the as-cast microstructure.

Solubility of oxygen in alloys of niobium with elements of Group IVA

(a) Niobium-zirconium. Alloys containing 10 at.% Zr and from 0.1 to 1.0 wt.% O_2 were prepared, and examined metallographically after being brought into equilibrium at 1000°C and quenched. An oxide phase appeared in all samples, subsequent X-ray work proving that this oxide was ZrO₂. The solubility of oxygen in niobium is therefore markedly reduced by zirconium, being less than 0.1 wt.% oxygen at 1000°C with 10 at.% Zr additions.

(b) Niobium-titanium. Since the solubility of oxygen was so markedly reduced by zirconium additions to niobium, it was decided to investigate the effect of titanium additions over a wider range of composition than possible with zirconium, the range of niobium-zirconium alloys studied having been restricted by the appearance of the hexagonal close-packed α -zirconium phase in oxygen-free alloys containing more than 10 wt.% Zr.

Results of metallographic work carried out on alloys containing up to 42 at.% titanium are set out in Fig. 6. Oxygen solubility is increased by titanium additions reaching a value of 0.75 wt.% at 40 at.% titanium. It was not possible positively to identify the phases present in the two and three phase regions in Fig. 6, but it is considered on limited X-ray information that these may consist of a hexagonal phase corresponding to the α -titanium structure, TiO and the b.c.c. niobium solid solution.



Fig. 6. Solubility of oxygen in niobium-titanium at 1000°C; Δ , two phases; \Box , three phases; O, single-phase samples.

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DISCUSSION

The solubility limit of oxygen in a metal is reached when the partial free energy of oxygen in the oxide phase formed in equilibrium with the solid solution is equal to the partial free energy of oxygen in solution; thus the measured solubility may be altered by a change in either of these variables. It has not been possible in this investigation to determine these two effects separately, nevertheless some conclusions may be drawn.

Some aspects of the results obtained could possibly be associated with a change in the equilibrium oxide. In niobium-rhenium alloys, for example, oxygen solubility is increased by small rhenium additions. This could be explained by an initial change in the oxide formed, the subsequent decrease being due to an overriding electronic effect. An inflection in the solubility curve for niobium-molybdenum alloys being 12 at.% and 35 at.% is perhaps less certainly associated with oxide changes.

Zirconium and titanium both have oxides which are more stable than the oxides of niobium², consequently it might be expected that oxygen solubility would be reduced even though the effect of dissolved titanium and zirconium might well be to increase the affinity of the metal for oxygen. In niobium-zirconium alloys this is in fact what was observed, solubility being low and ZrO₂ being formed. In niobiumtitanium alloys, although TiO, which is more stable than NbO, is formed, the measured oxygen solubility is increased, indicating that titanium additions increase the affinity of the solid solution for oxygen.

Much evidence already exists which indicates that the *d*-band of transition elements may be split into sub-bands. JONES et al.³ found that the paramagnetic susceptibility of titanium-molybdenum alloys and niobium-molybdenum alloys show minima at electron to atom ratios between 5.6 and 5.7, and also that hydrogen solubility fell to zero in titanium-molybdenum alloys at an electron to atom ratio of 5.6, also the Hall coefficient of titanium-molybdenum alloys shows a maximum at an electron/ atom ratio of about 5.64.

In the present work in alloys of niobium with molybdenum, rhenium and ruthenium, oxygen solubility falls effectively to zero at 75 at.%, 35 at.% and 25 at.% respectively. It is thus clear that in each of these cases zero solubility is reached at electron to atom ratios between 5.70 and 5.75, and further confirmation of sub-band filling at this electron concentration has been obtained. It is interesting to note that the electron/atom ratio for zero solubility is very little different even when an element from Group VIII is added, indicating that the position of the break in the *d*-band is not very much changed by the elements present but controlled primarily by the electron/ atom ratio. The close parallel between oxygen and hydrogen solubilities is interesting since from the present results it may be concluded that oxygen in solution is to a certain extent positively charged and not negatively charged as commonly supposed, since oxygen solubility is reduced by increasing the electron concentration.

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