Oxidation of High Temperature Titanium Alloys

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Abstract

The oxidation behaviour of commercially pure titanium has been compared with that of a conventional high temperature titanium alloy and an α_2 titanium aluminide. Isothermal oxidation tests have been performed on IMI125, IMI834 and "Super α_2" over the temperature range 600 to 900°C. The development, compositions and morphologies of the various scales produced have been examined using X-ray diffraction, Auger electron spectroscopy and analytical electron microscopy to establish the nature of the oxides formed and the chemical partitioning which occurs in both the substrate and the scale. Microhardness measurements have been used to determine the depth of penetration of oxygen into the alloys during oxidation. Preliminary results from oxidation trials on Ti-48Al-2Nb-2Mn are also presented. The observations show that the oxidation rate is a complex function of oxidation temperature and alloy composition. It appears that oxidation is controlled by the kinetics of competing mechanisms rather than by minimum energy considerations.

Titanium '92
Science and Technology
Edited by F.H. Froes and I. Caplan
The Minerals, Metals & Materials Society, 1993

Introduction

The use of conventional titanium alloys is limited to temperature regimes below about 600°C because of their oxidation behaviour which proceeds via the inward diffusion of oxygen to produce thick oxide scales, and results in a pronounced degradation in mechanical properties associated with the dissolution of oxygen in the titanium matrix. Oxygen is soluble in α-titanium up to 34 atomic% and is α-stabilising which leads to severe embrittlement in the oxygen-enriched surface layer of the material.

Whilst it is known that various alloying additions to pure titanium have a beneficial effect on its overall rate oxidation it would seem that the basic mechanism remains the same with both oxide scales and α-case being formed simultaneously. It is obvious that in order to effect a further increase in the high temperature capabilities of titanium alloys, either through compositional control or by some method of coating, it will be essential to gain a better understanding of the role of the individual alloying elements on the oxidation behaviour of these materials.

Titanium aluminide materials have potential for high temperature applications and are superior to titanium alloys in terms of oxidation resistance [1].The use of aluminides may however also be limited by their poor resistance to oxidation above about 600°C (α_2-alloys) and 900°C (γ-alloys) [2]. The basic principles of loss of structural material by oxide scale formation and surface embrittlement apply equally to the oxidation of the titanium aluminides. Scales produced are heterogeneous mixtures of TiO_2 and Al_2O_3, and again additional elements such as Nb have a beneficial effect on the rate of oxidation [3].

The aim of the present study is to compare high temperature oxidation studies of IMI834, "Super α_2" and Ti-48Al-2Nb-2Mn with that of commercially pure titanium and more clearly define the behaviour of their key alloying additions.

Experimental Details

Specimens of IMI125, IMI834 and Super α_2 were prepared in the form of 10mm diameter discs of 1mm thickness. These were mechanically polished to 800 grit SiC paper and degreased prior to oxidation. The specimens were then isothermally exposed in air at temperatures from 600 to 900°C for 100h, using a Stanton Redcroft Thermobalance. Morphological studies of the oxides were carried out using a Cambridge scanning electron microscope (SEM), Auger analysis (AES), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD) studies were also done on these specimens and on samples of spalled oxides. Table I shows alloy compositions. Cross-sections of oxidised specimens were prepared for microhardness traverses and oxide thickness measurement by SEM examination. Transmission electron microscopy (TEM) was carried out on cross-sectional specimens of oxidised material produced by glueing together two disc specimens of 1.5mm thickness using an epoxy resin. These were then sectioned to produce a rectangular specimen of 3mm x 3mm x 10mm, which was carefully filed down until small enough to be encapsulated in a thin walled brass tube of 3mm outside diameter. Sections of 0.3mm thickness were cut from the specimen and were mechanically polished to 100-150μm before being dimpled to less than 50μm using an SBT Precision Dimpling Instrument. The thin discs were finally ion milled for TEM examination which was carried out on either a JEOL 4000FX or a Philips CM20.

TABLE I Composition of the alloys

Material	Composition (wt %)
IMI125	Ti - 0.13 O_2
IMI834	Ti -5.8Al - 4Sn - 3.5Zr - 0.7Nb - 0.5Mo - 0.35Si.
Super α_2	Ti - 14Al - 20Nb - 3.2V - 2Mo.
48-2-2	Ti - 48Al - 2Nb - 2Mn.

Results

Figure 1 shows weight gain data for commercial purity Ti (IMI125), IMI834, Super α_2 and Ti-48Al-2Nb-2Mn, which include corrections due to buoyancy effects. Double logarithmic plots of this data allow evaluation of n, the exponent for oxidation according to the equation:

$$\Delta W^n = Kt + C \tag{1}$$

where ΔW is weight gain ($mgcm^{-2}$), K is the constant of oxidation, t is time and C an integration constant.

IMI125 shows parabolic kinetics at low temperatures after extended times, and at high temperatures, but linear kinetics at intermediate conditions. Discontinuous curves are indicative of para-linear behaviour which is usually associated with the repeated cracking and spalling of scale followed by rapid oxidation. IMI 834 exhibits a low linear rate of oxidation after exposure at 700°C, but rates tend towards parabolic at 800-900°C. Super α_2 is found to have a low linear rate of oxidation at 600°C, at 700°C a linear rate prevails up to 20h after which kinetics tend towards parabolic. Parabolic behaviour is found at 800-900°C. Ti-48Al-2Nb-2Mn has a low linear rate of oxidation at 800°C, and cubic oxidation rates at 900°C.

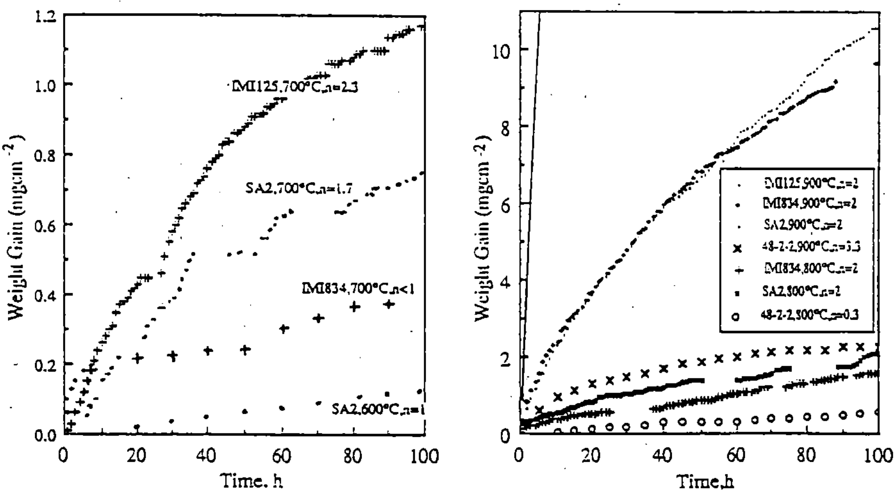

Figure 1. Isothermal Oxidation Curves of Weight Gain (ΔW) versus Time (t) for IMI125, IMI834, Super α_2 and 48-2-2

In general the results obtained between 600°C and 900°C show the beneficial effect of alloying on the oxidation resistance of titanium although overall weight gains are higher for Super α_2 than for IMI834. For both alloys the temperature range over which parabolic kinetics are observed is extended towards higher temperatures when compared with unalloyed titanium. The initial oxidation rate (less than 10h), for IMI834 at 700°C however is actually faster than that of IMI125. The observed reversion of IMI125 to parabolic kinetics at 900°C is attributed to the densification of the scale adjacent to the substrate, thus the diffusion of oxygen through the scale rather than along micro-cracks and porosity, becomes rate controlling.

SEM and Auger Spectroscopy of oxide scales

SEM observation of oxidised pure titanium, figures 2 and 3, show that the porous scale, formed at 700°C, develops into a uniformly stratified scale after oxidation at 800°C. The stratification begins to disappear at 900°C by sintering and densification of the scale adjacent to the metal substrate. The surface oxide grains are quite angular and faceted after oxidation at 900°C. Scales at all temperatures have very poor adherence.

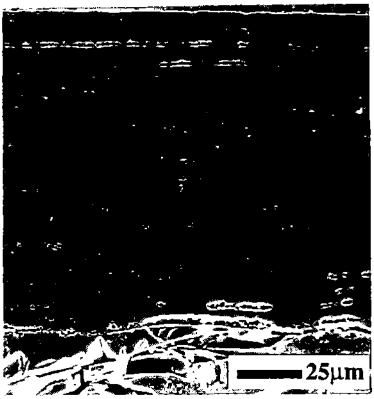

Figure 2. SEM micrograph of oxide on IMI125 after 100h at 800°C.

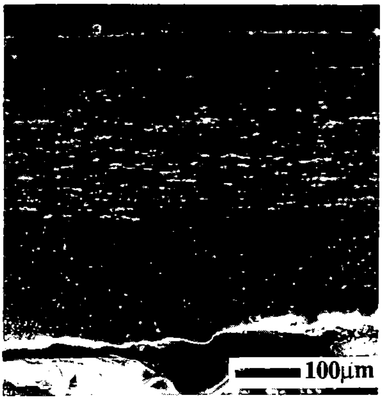

Figure 3. SEM micrograph of oxide on IMI125 after 100h at 900°C.

Fine needle-like oxide crystals are formed on the surface of IMI834 after oxidation at 600°C, which develop into faceted columnar grains at higher oxidation temperatures. At 900°C the oxide scale, figure 4, comprises a coarse grained surface layer of approximately 7μm, a compact but stratified oxide of about 55μm and a thin porous layer at the metal:oxide interface. The oxide remains reasonably adherent up to 800°C, above this the deep yellow outer oxide readily spalls to reveal a dark blue/grey adherent oxide. X-ray diffraction (XRD) of the scale formed at 600°C found only "TiO_2". Scale formed at 900°C was found to be a mixed oxide of "TiO_2"and "Al_2O_3". It should be noted that these oxides are likley to be doped with alloying elements, however their concentration is below the limit of detectability in the techniques used here.

Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) of IMI834 have been used to analyse the oxide scale and the metal:oxide interface. Both Al_2O_3 and SiO_2 were detected in a predominantly TiO_2 oxide scale. It would appear that there is a very thin layer of Al_2O_3 on the surface of the scale, of the order 150Å. An AES depth profile, figure 6, showed that a possible layer of SiO_2 is removed after etching for approximately 4 minutes, which suggests that the thickness of the layer is about 0.15μm [4]. Al_2O_3 and SiO_2 are found in small concentrations throughout, and analysis of the fractured scale suggests that there is some concentration of Al_2O_3 along the cracks and that SiO_2 is found in greatest concentration at the metal:oxide interface.

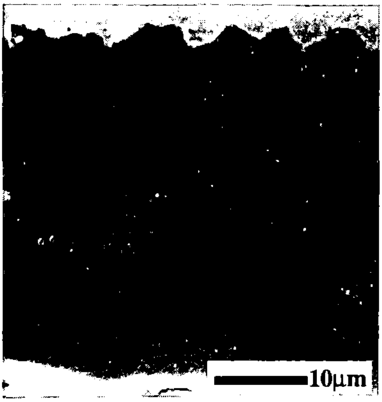

Figure4. SEM micrograph of oxide on IMI834 after 100h at 900°C.

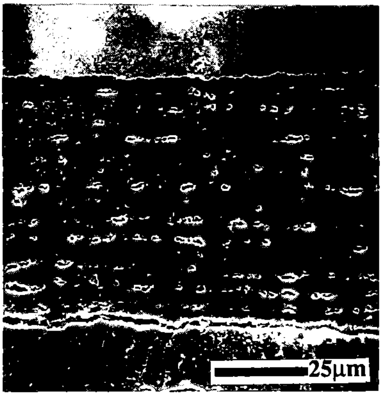

Figure 5. SEM micrograph of oxide on Super α_2 after 100h at 900°C.

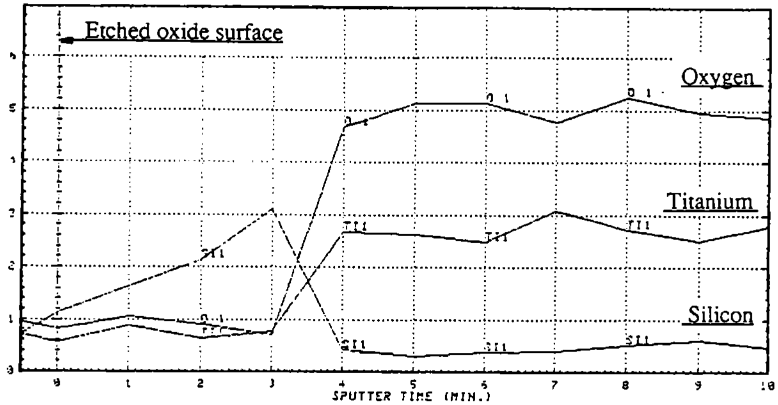

Figure 6. AES Profile through surface of scale formed on IMI834 after 100h at 900°C.

The oxide formed on Super α_2 remains adherent up to 900°C. This oxide, Figure 5, consists of uniformly thick layers in which grains are rounded and equiaxed. The total thickness of the oxide is ~ 75µm. Beneath this layered oxide, adjacent to the metal substrate, there is a dark, thin, adherent oxide. XRD analysis of the specimen detects TiO_2 with only small amounts of Al_2O_3. AES showed that the scale formed at 900°C consists of TiO_2 and Al_2O_3 with trace amounts of Nb and V. A depth profile through approximately 0.5µm of the scale from the surface showed very little change in composition except for an apparent reduction in the V signal after etching the surface.

Oxide thickness measured by SEM examination of cross-section specimens, shows that scales formed on the alloys are not only considerably thinner than those formed under equivalent conditions on titanium, but are also more compact and stratification is less distinct thus preventing easy access of oxygen to the metal surface and diffusion-controlled kinetics are maintained. Alpha-case depths above 600°C, are also considerably thinner in the alloys than in the unalloyed material. Below 800°C there is negligible difference between the two alloys. There is however, a rapid increase in the alpha-case on IMI834 above 800°C, which is likely to be caused by the loss of scale adherence, hence permitting the rapid ingress of oxygen to the exposed surface. The scale thickness on Super α_2 increases with respect to that of IMI834 above 800°C, but remains strongly adherent even after oxidation at 900°C.

Cross sectional TEM of oxidised samples

Cross-sectional TEM has been carried out on specimens of IMI125 and IMI834 oxidised at 600°C for 100 h, figure 7. Measurements of the scale thickness and the appearance of distinct oxide layers is consistent with SEM observations. The alloy scale consists of a compact layer about 2nm thick, which is found next to the substrate, a more porous layer of 50nm and a coarse surface oxide of about 150nm. EDX has not shown any major differences in composition in the oxide on IMI 834.

Selected area diffraction of the scales gives a series of ring patterns, which have been indexed and identified as TiO_2. No cross sectional specimen of Super α_2 has been produced as yet but extensive further work is planned.

Measurement of oxygen penetration depth from hardness profiles

Hardness measurements have been made on oxidised samples which were cross sectioned after oxidation at 600 and 900°C. Assuming that oxygen concentration is directly related to hardness of the material, hardness profiles reflect the relative oxidation rates of the alloys at the different temperatures. The penetration is greatest in IMI125, and least in Super α_2. At lower temperatures the behaviour is not as systematic, as pointed out from the weight gain observations, and it appears that short circuit diffusion paths influence oxidation at these lower temperatures. Diffusion coefficients for volume diffusion of oxygen in the matrix materials are presented in the form of an Arrhenius relation in figure 8.

Figure 7. TEM micrograph of cross-section oxide on IMI834 after 100h at 600°C.

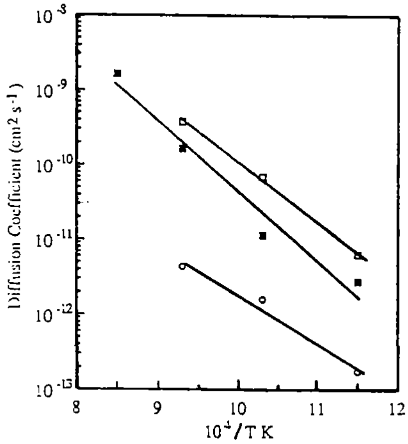

Figure 8. Diffusion coefficient for oxygen in IMI125, IMI834 and Super α_2.

Discussion

The interpretation of the results obtained in this work is not straightforward and it is clear that not only are different factors important at different temperatures but it is also clear that kinetic factors are involved as well as minimum energy considerations. The fact that there are changes of mechanisms with change of temperature is well illustrated by the weight gain experiments where the relative rates of the samples changes between 600 and 900°C. This immediately raises difficulties in determining the activation energies of the processes which are rate-controlling as will be discussed below.

The importance of factors, other than minimum energy considerations is apparent from the Auger observations where it has been found that alumina is formed in the oxide both on IMI834 and on Super α_2. It has been found that the concentration of Al needs to be above about 57-59 at% before a continuous Al_2O_3 scale is oxidised from Ti alloys [5]. The Al contents of the alloys investigated here are well below this and Al is present in small concentrations throughout the scales on both of the alloys, in the form of α-Al_2O_3. The presence of Al must therefore involve a mechanism other than that dictated by the relative activity of Ti and Al. If, as seems likely, Ti is indeed oxidised first to form TiO_2, or some sub oxide, there will be an increase in the Al concentration at the oxide metal interface, unless the Al diffuses away from this interface into the body of the metal. If Al is simply incorporated into the advancing oxide, there could be significant build up of Al in the oxide. Subsequent oxidation of the Al would lead to the formation of Al_2O_3 and this would lead to a reduction in the oxidation rate in IMI834 and Super α_2 as compared with that in IMI125, as observed. In addition the formation of Al_2O_3 could slow the oxidation rate down to such an extent that the diffusion of oxygen into the body of the metal could now be controlled by the rate of arrival of oxygen at the metal-oxide interface and this would influence the oxygen penetration depth as measured using hardness measurements.

On the basis of the Wagner-Hauffe theory of mass transport in oxides Al^{3+} cations present in the anion deficient TiO_{2-x} lattice should increase the number of oxygen vacancies and thus cause an increase in the rate of oxygen transport through the oxide. This however, is not observed experimentally and it should be noted that the presence of pentavalent cations in the alloy readliy compensate for this effect. Other mechanisms must be operative as mentioned above; an effect of Al occupying interstitial positions in the TiO_2 [6], or simply the trapping of diffusing oxygen atoms by the Al atoms, would result in the reduction in the rate of oxidation.

The Auger analysis of oxidised Super α_2 detected trace amounts of Nb and V in the $TiO_2 + Al_2O_3$ scale, however it is not obvious that such small concentrations could have a significant effect on the oxidation rate. The Wagner-Hauffe theory predicts that the substitution of Nb^{5+} and V^{5+} into the TiO_2 lattice would cause a reduction in the number of oxygen vacancies and hence a reduced rate of oxidation. Again since this effect is very small and easily compensated by other alloying elements, some other mechanism of reducing the oxgyen flux must be operative. Nb_2O_5 scale formed on Nb is very porous and offers little resistance to oxidation, however it is the most stable of the Nb oxides in this system, and can form complex oxides with TiO_2 and Al_2O_3 [3]. These compounds being relatively dense are more protective, than the porous TiO_2-Al_2O_3 scale.

In contrast to the activity argument for the formation of Al_2O_3, the concentration of SiO_2 at the metal:oxide interface on IMI834 is not surprising since the free enthalpy of formation of SiO_2 is smaller than that of TiO_2. The presence of smaller concentrations of SiO_2 detected throughout the scale is consistent with cation diffusion towards the oxygen:oxide interface. Si is thought to play an important role in the prevention of oxygen dissolution into the metallic substrate [7], although the mechanism for this is not clear. It would appear however, that its presence at the interface has a detrimental effect on the adherence of the scale at the higher temperatures. This is in agreement with the findings of [8] who report that small concentrations (less than 0.5 wt %), reduce scale adhesion when compared to pure Ti. The Pilling-Bedworth ratio of SiO_2 (1.88-2.15) is significantly larger than that of TiO_2 (1.73); this difference in molecular volume between the two oxides and the metal will cause an increase in stress at the interface.

Cracking and spalling of the oxide make it very difficult to determine the rate controlling factors that govern oxidation from measurements of the oxide thickness. The data collected in the present work has shown that over some ranges of temperature the oxidation, as measured by weight gain is parabolic. Since the weight gain is due to oxygen which has diffused to form both oxide and oxygen-rich surface layers it is a measure of the total rate of oxygen take-up. The temperature dependence of the weight gain, when the kinetics are diffusion-controlled (ie. when the gain is parabolic with time) could be used to determine the activation energy over that limited temperature range. Unfortunately the data obtained do not show smooth parabolic weight gain over a sufficient temperature range to allow such an analysis.

It is tempting to consider whether the hardness data, which measures the oxygen penetration into the samples can be used instead to determine the rate controlling factors. On the assumption that the rate controlling factor is the diffusion of oxygen through the alloy, and that the diffusion of oxygen through the growing oxide does not influence the rate of penetration, the diffusivity of oxygen in the alloy can be measured from the hardness measurements. Thus the diffusion distance at each temperature is given by $x = \sqrt{Dt}$ so that D can be obtained as a function of temperature. Figure 6 shows a plot of D against $10^4/T$ which allows the determination of D_o and Q defined in the equation

$$D = D_o \exp(-Q/RT) \qquad (2)$$

Values of D_o and Q obtained from these results, on the assumption there is a singly activated event controlling oxygen penetration in the metal, are presented in Table II.

TABLE II Diffusion Coefficients and Activation Energies from hardness profiles (Hv)

Material	Q, kJ $mole^{-1}$	D_o, $cm^2\ sec^{-1}$
IMI125	155	1.4×10^{-2}
IMI834	180	1.0×10^{-1}
Super α_2	121	4.6×10^{-6}

The values of D_0 and Q obtained for IMI125 and for IMI834 are comparable with published data [9] and appear to be physically reasonable. The data obtained for Super α_2, however, give values of Q and D_0 which do not seem to be physically reasonable. Earlier analysis has shown [10] that very low values of D_0 are not compatible with singly activated events. Various suggestions have been put forward to account for such low values but from the present viewpoint it is reasonable to conclude that equation (2) does not appear to describe diffusion through Super α_2.

The oxidation behaviour of titanium alloys at high temperatures and the role of additional elements is complex. Further work is required to understand all contributing factors, a fact reflected in the wide divergence in reported data. It may not be appropriate to use a simple Arrhenius relationship to characterise the kinetics; a more detailed examination of all the mechanisms of diffusion involved in the oxidation process is necessary. The improvement in oxidation rate of the alloys over that of pure titanium may be attributed in part, to the improvement in the barrier properties of the scale. Cation diffusion through the scale seems a likely mechanism of reducing the flux of oxygen to the metal interface. An important factor in scale adherence is the build up of stresses at the metal-oxide interface; the influence of alloying additions concentrated in this region on oxide spalling characteristics merits further investigation. Furthermore, additional cross-sectional TEM examination is considered important to the understanding of the oxidation behaviour of these materials.

Acknowledgements

The authors would like to thank Professor J.F. Knott, Head of the School of Metallurgy and Materials, for the provision of laboratory facilities and, IMI Titanium and SERC for their financial support. Dr Charles Younes of The Interface Analysis Centre, Bristol University is also gratefully acknowledged for the provision of Auger facilities and for many useful discussions.

References

1. M. W. Kearns, "High Temperature Oxidation of Binary and Ternary Titanium Aluminides", (Paper presented at Conference"Production and Applications of Less Common Metals", Hangzhov, China, 8 November, 1982).

2. H. A. Lipsit, "Titanium Aluminides-An Overview", High Temperature Ordered Intermetallic Alloys, Mater. Res.Soc. Symp. Proc., 39, (1989), 351-357.

3. G. Welsh and A. I. Kahveci, "Oxidation Behaviour of Titanium Aluminide Alloys", Oxidation of High-Temperature Intermetallics, (Cleveland, OH: The Minerals, Metals and Materials Society, 1989), 207-218.

4. C. M. Younes and T. J. Johnson, Unpublished work.

5. G. H. Meier and D. Appolonia, "Oxidation of Ti-Based Alloys", Oxidation of High Temperature Intermetallics, (Cleveland, OH: The Minerals, Metals and Materials Society, 1989), 185-193.

6. K. S. Forland, Acta Chem. Scand., 20, (1966), 2573.

7. A. M. Chaze and C. Coddet, Journal of Materials Science, 22, (1987), 1206-1214.

8. A. M. Chaze and C. Coddet, Oxidation of Metals, 28,1/2, (1987),61-71.

9. Z. Lui and G. Welsh, Met. Trans. A, 19A, (1988), 1121-1125.

10. R. P. Agarwala, S. P. Murarka, M. S. Anand, Acta Met., 12, (1964), 871-874.