

Surface Segregation of Sulfur in Ti and Ti-Aluminide Alloys

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티타늄과 티타늄 알루미늄아이드 합금에서 황의 표면석출

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Abstract – The segregation of S in electrotransport-purified polycrystalline α -Ti and Ti-aluminide alloys has been studied by Auger electron spectroscopy(AES), Ion scattering spectroscopy(ISS) and Secondary ion mass spectrometry(SIMS) in the temperature range extending from 20 to 1000°C. The chemisorbed oxygen and carbon on Ti were observed to disappear at $T > 400^\circ\text{C}$ after which the S signal increased to levels approaching 0.5 monolayer. At lower temperatures the presence of the surface oxygen and carbon appeared to inhibit the segregation, presumably because there were no available surfaces sites for the S emerging from the bulk. The activation energy for the S segregation in pure polycrystalline Ti was determined to be 16.7 kcal/mol, which, when compared to S segregation from single-crystal Ti, is quite small and suggests grain boundary or defect diffusion segregation kinetics. In the Ti-aluminide alloys, the presence of Al appeared to enhance the retention of surface oxygen which, in turn, substantially reduced the S segregation. The γ alloy, with its high Al content, exhibited the greatest retention of surface oxygen and the smallest quantity of the S segregation($T \approx 1000^\circ\text{C}$).

요 약 – Auger electron spectroscopy(AES), ion scattering spectroscopy(ISS), secondary ion mass spectrometry(SIMS) 등을 사용하여 시료의 온도를 20°C에서 1000°C까지 변화시키면서 고순도 Ti 다결정과 Ti-aluminide 합금에서 황의 표면석출 현상을 조사했다. 400°C 이상에서 Ti 다결정 표면의 산소, 탄소 성분은 사라지고 황 성분은 0.5 단층까지 증가되었다. 400°C 이하에서는 표면의 산소와 탄소가 황이 표면석출될 자리를 점유함으로써 황의 표면석출 현상에 큰 영향을 주었다. 다결정 Ti에서 황의 표면석출 활성화 에너지는 단결정 Ti에서 황의 표면석출 활성화 에너지보다 아주 적은 16.7 kcal/m이었다. 따라서 다결정 Ti에서 황의 표면석출은 결정경계나 결함 확산기구를 따른다고 생각한다. Ti-aluminide 합금에서는 알루미늄이 표면으로 석출되어 높은 온도에서도 산소를 표면에 보유함으로써 황의 표면석출 현상에 영향을 주었다. 알루미늄의 양이 비교적 많은 γ 합금인 경우 1000°C 근방에서도 표면에 많은 양의 산소가 존재했으며 이로 인하여 표면에 석출된 황의 양도 가장 적었다.

1. Introduction

Ordered intermetallic compounds such as the Ti-aluminides are being considered for use in hypersonic flight vehicles because of their high strength-to-weight ratio, their high elastic modulus, and their high temperature, creep-rupture strength. Metastable β -titanium alloys are also candidate ma-

terials for Ti matrix composite structures in hydrogen-fueled hypersonic planes because of their excellent formability and mechanical properties in the 500-800°C range^{1, 2}.

Unfortunately, the segregation of S at high temperatures can significantly degrade the properties of these materials. The segregation of S is frequently observed in many different systems, such as Fe, Cr,

Ni and all the steels, and results from the dissolved S aggregating at the grain boundaries and defects when the material is raised to elevated temperatures [3-15]. This can result in decreased ductility and increased fracture probability. Ultimately, the S can diffuse to the free surface or interface where it spreads to some concentration, dependent on the surface conditions and the concentration gradient. The presence of the S at the surface may be an innocuous nuisance, a poison to a catalytic surface, or actually weaken the bonding at an interface, such as the spalling of an Al_2O_3 coating on Ni-based superalloys [14, 15]. The segregation of S in metals and their alloys usually proceeds by volume diffusion (activation energy, E_v) from the bulk to the grain boundaries and defects, by grain boundary diffusion (activation energy, E_{gb}) to the surface, and then by surface diffusion (activation energy, E_s) to spread over the interface. The diffusion coefficient ordinarily increases for each respective step, and the activation energy is usually in the order $E_v > E_{gb} > E_s$, but these rates are ultimately controlled by mechanism-specific constraints. In the bulk, for example, the atoms are usually located in interstitial, substitutional, or defect sites, and the activation barrier is defined by the jump resistance to the next site. In the grain boundary, the sulfur may be more mobile in a more open structure but may be blocked by other atoms (and their associated diffusion rate).

On the surface, the native adsorbate may be strongly bound to the surface sites and S segregation not occur until the adsorbate dissolves or desorbs, leaving sites available. In the past, very little research on Ti alloys has been done to characterize this phenomenon, so the purpose of this paper is to present a study of the S segregation observed in the vacuum processing of α -Ti and the aforementioned Ti alloys over the temperature range from room temperature to 1000°C.

2. Materials

The materials studied in this work are: α -Ti, Ti-

14Al-21Nb(α_2) and Ti-33Al-6Nb-1.4Ta(γ). The samples were fabricated in the shape of a 5 mm square, 0.2 mm thick wafer. The microstructure of the electrotransport-purified [9] α -Ti was equiaxed α grains, that of the Ti-14Al-21Nb was equiaxed α_2 grains with small amounts (20%) of a β phase located at the grain boundaries, and that of the Ti-33Al-6Nb-1.4Ta was γ grains (90%) with a fine dispersion of α_2 precipitates. The bulk content of the sulfur in these materials was determined by plasma-inductive coupling and found to be : α -Ti (1.5 wppm), α_2 (135 wppm) and γ (29 wppm). Prior to introduction into the surface analysis system, the samples were sequentially degreased, polished to 2000 grit, chemically cleaned (25% HNO_3 , 2% HF), rinsed several times in de-ionized water and hot-air dried. The samples were then installed in the introduction chamber and eventually transported into the analysis chamber.

3. Experimental

The experimental system includes Auger electron spectrometry(AES), ion scattering spectroscopy(ISS), secondary ion mass spectrometry (SIMS) and quadrupole mass spectrometry(QMS). The AES data were obtained with a cylindrical mirror analyzer(CMA) operated with a 10kV coaxial gun at an energy of 3 keV and a beam current of 1 μ A. The ISS data were taken using low flux beams of He+ (to minimize surface desorption) in forward and back scattering modes. During the ion scattering experiments the normal operating pressure was around 4×10^{-8} torr. It allowed ion bombardment in the energy range from 100 to 5000 eV with ion current density of around 10^{-8} A/cm² with noble gas ions He⁺, Ne⁺ or Ar⁺.

The SIMS consisted of a four gridded energy analyzer with an energy resolution of less 0.5 eV and with a detector dark noise of less than 0.5 cps couple to a QMS. During the SIMS experiments the normal operating pressure was around 4×10^{-8}

torr. It allowed ion bombardment in the energy range from 100 to 5000 eV with ion current density of around 10^9 A/cm² for the static SIMS mode with noble gas ions Ne⁺ or Ar⁺. The secondary ions were first energy analyzed in a four-gridded energy analyzer and then mass-filtered by means of a QMS and detected by an open channel electron multiplier. Both the scattered ion intensity in ISS and the sputtered (secondary) ion intensity in SIMS were recorded by the ratemeter through the timing amplifier with four stage and 100MHz discriminator.

The base pressure in the system was approximately 2×10^{-11} torr. The samples were first introduced into a load/lock preparation chamber (where they could be vacuum fired or processed in a desired atmosphere up to 1000°C), evacuated to 1×10^{-7} torr or less; and then transferred into the analysis chamber manipulator. The samples in the manipulator could be heated to 1000°C and positioned in front of any diagnostic system in the analysis chamber. Most AES spectra were taken at room temperature, but spectra at the experimental temperature were also taken to ensure there was no difference. The as-received samples were heated in-situ to the test temperature and maintained there for 30 min, and then the spectra were taken. The samples were then cooled to room temperature and spectra taken again. This procedure was repeated in 100°C increments from room temperature to 1000°C. The segregated sulfur was Ar⁺ sputtered away, and then the samples were dosed to saturation with O₂ and the experiments repeated.

The atomic concentration of the surface was ascertained from the $d[E \times N(E)]/dE$ spectrum by using published Elemental Sensitivity Factors (ESF) [16] and peak-to-peak height measurements. Concerns about instrument fluctuations and over-layer effects are resolved by normalizing all peaks to the dominant stable feature; the Ti 387 eV peak. The concentration of element χ is given by:

$$C_x = I_x / \text{ESF}_x / [\sum(I_\alpha / \text{ESF}_\alpha)],$$

where C_x is the atomic concentration of element χ , I_x is the peak-to-peak height of AES signal from element χ , I_α is the peak-to-peak height of AES signal from element α , ESF_x is the elemental sensitivity factor of element χ and ESF_α is the elemental sensitivity factor of element α , and the summation is over one peak per element.

4. Results and discussion

4.1. α -Ti

The AES spectra for the pure, as received α -Ti is shown in Fig. 1(a). Since the chemical reactivity for the IVB group is so great, atmospheric gettering generated a substantial oxygen and carbon contamination layer. The source of the high initial concentration of O and C is from adsorbed gases, such as H₂O, CO, and CO₂. After Ar⁺ sputtering, the oxygen and carbon signals were greatly reduced, but still present because of the continual uptake of background gases. In the as-received sample, the O was in the form of TiO₂, as indicated by the O KLL (510 eV) peak height and by the peak shapes and energy shifts of the TiL₁M_{2,3}M_{2,3} (383eV), the TiL₁M_{2,3} V-shakeup (387 eV), TiL₁VV (451 eV) transition peaks [17]. The thickness of the native oxide can be determined from the increase in TiL₁M_{2,3}V (387 eV) following the incorporation of the surface oxygen. Using the mean-free path for 387 eV Auger electrons in the TiO₂ layer, the thickness was found to be 1.8 nm, which is consistent with other native oxides [18, 19]. Upon heating, the oxide was found to be relatively stable until 450°C where the surface concentration of the O dropped sharply to less than 5% at 600°C [9-11]. The disappearance of the surface species proceeded by either dissolution into the bulk or by desorption as CO, CO₂ or SO₂. No increase in the QMS signals was observed to occur in the temperature region where the oxygen and carbon disappeared, so dissolution

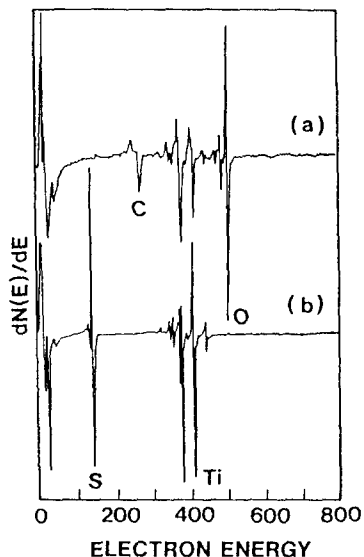


Fig. 1. (a) AES survey of the as-received electrotransport-purified α -Ti showing the predominant oxygen (TiO_2) and carbon (amorphous) contaminants. (b) The α -Ti after heating in UHV at 800°C for 30 min. Note the complete disappearance of the O and C and the dominant appearance of S.

into the bulk is the most likely mechanism. At $T = 700^\circ\text{C}$, the O had completely disappeared from the surface. The C present, although a much smaller quantity than the O, had also disappeared by 700°C [8]. After heating the sample to 800°C , no other contaminant was observed except sulfur. Fig. 1(b) shows the very large sulfur LVV(152 eV) peak and the absence of oxygen and carbon after 30 min at 800°C . It is important to note that this data represent only AES indications which do not accurately indicate the top-most layer. The ISS (which is much more sensitive than AES) taken on this same surface a few minutes later, showed that there was still some oxygen detectable on the Ti at $T=700^\circ\text{C}$, even though no AES signal was observed. This can be explained by gettering of the background contaminant gases, however.

A plot of the segregation of sulfur as a function of temperature is presented in Fig. 2. Maximum sulfur accumulation, as determined by Ti signal attenuation and mean-free-path techniques, ap-

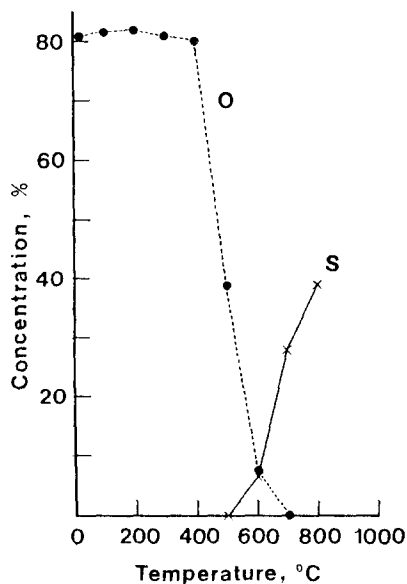


Fig. 2. Variation of S as a function of temperature for the as-received α -Ti. The dashed line represents the corresponding dissolution of the surface oxygen. Each data point was taken after 30 min. at each temperature.

proached that of 0.5 monolayers[18]. The S segregation in the as-received samples was not observed until 500°C and then dramatically increased to the magnitude shown in Fig. 1(b). The dashed line represents the disappearance of the oxygen during this same run, indicating somewhat of a mirror image. This suggests that the oxygen, and perhaps the carbon, constrained the S to remain in the bulk until the dissolution of the O and C occurred. The desorption of SO_2 was not observed in the QMS during heating cycles. If significant S were desorbing into the gas phase with the oxygen, it would suggest that S spread over the adsorbed O, which is highly unlikely given the well known site competition[13].

Fig. 3 shows the variation of the S and Ti (418 eV) Auger peaks normalized to Ti (383 eV) peak as a function of sputtering time at 400°C after surface sulfur concentration was maximized by heating at 800°C for 2 hours. The peak height of the Ti(418 eV) is independent of the amount of the

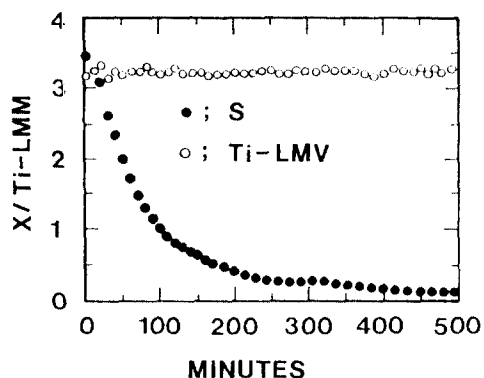


Fig. 3. Variation of S Auger peaks normalized to Ti (383 eV) peak as a function of sputtering time at 400°C for -Ti after heating in UHV at 800°C for 2 hours.

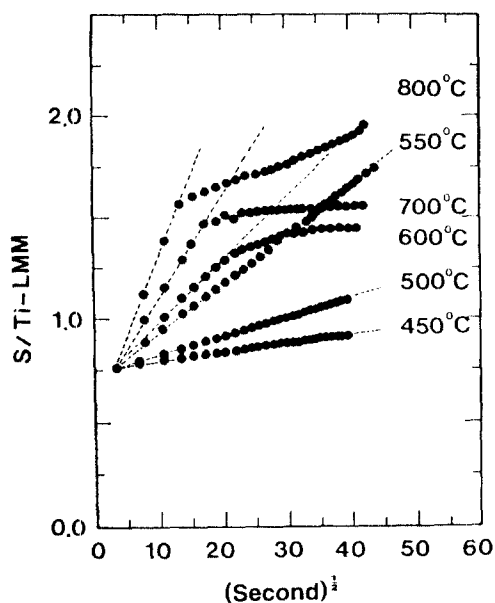


Fig. 4. Rates of segregation of S, normalized to the TiLMM peak, plotted as a function of $t^{1/2}$ over the range of temperature 450-800°C.

surface sulfur. No change of the peak shape and no energy shift of the Ti(418 eV) is observed. These results suggest that the surface bond of the S is a tenuous one. An exposure of Ar⁺ sputtering completely removed the S whereupon the O and C immediately began to reappear on the surface at a

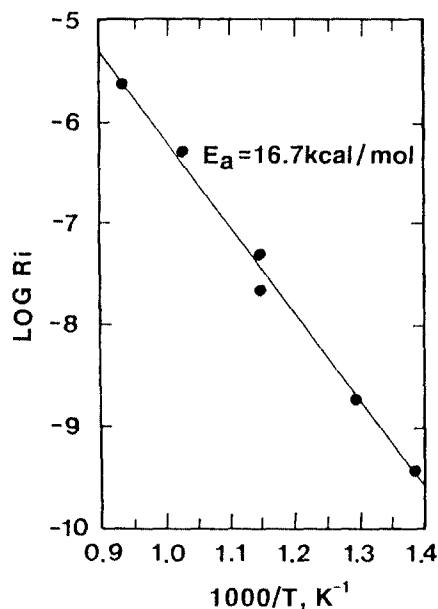


Fig. 5. Arrhenius plot of the initial rates (R_i) in Fig. 4 indicating a small activation energy of 16.7 kcal/mol.

rate commensurate with the partial pressure of the background gases. No peak shape variation or energy shift of the S transition was observed. High-pressure exposures of oxygen ($p \approx 760$ torr) at room temperature did, however, remove the sulfur.

Fig. 4 illustrates the variation of the sulfur AES peak normalized to the TiL_{2,3}M_{2,3}(383 eV) peaks as a function of the square root of time at temperatures from 450 to 800°C after sputtering. At all temperatures, the S concentration initially increased linearly as a function of $t^{1/2}$. The data at 450°C and 500°C stayed in the linear regime over the time period studied, and the data at 600°C and 700°C tailed off and began to approach a saturation value, possibly because of the S accumulation on the surface[20]. Similar behaviour has been observed with S segregation in Fe-6Si (100) where the rate versus $t^{1/2}$ was linear[12]. This process is a function of two different rates; the diffusion of S up the grain boundaries (or defects) and the diffusion of the S onto the surface. Except for the data at 800°C, extrapolation of these data

do appear to extend toward a saturation value. The data at 800°C ultimately begins to increase again, perhaps indicating spreading over grains not energetically favorable at lower temperatures [21].

An Arrhenius plot of the initial grain-boundary kinetics is shown in Fig. 5 and gives a value of $E_s = 16.7$ kcal/mol. This is much less than 21.2 kcal/mol found by Khan on a Ti(0001) single-crystal sample[7]. Although there is not nearly enough precision to speak conclusively, it does, however, indicate a trend. The lower activation energy in our work can be explained by a grain boundary diffusion component that is not available in the single-crystal work. Lofton and Swartz have measured the grain boundary transport of S in arc-melted Ti and reported the activation energy to be 18.7 kcal/mol[8]. The small difference in the activation energy between their work and ours may be due to impurity blockage in the grain boundaries coming from a less pure material than the electrotransport-refined Ti used in the present study. In either case, the magnitude of the activation energy is quite small and suggests that the segregation occurs readily as long as there is no surface barrier due to the occupied sites.

4.2. Ti-14Al-21Nb(α_2) and Ti-33Al-6Nb-1.4Ta(γ)

The addition of Al and Nb to the Ti substantially altered the surface composition as a function of temperature. The presence of Al was especially significant in the kinetics of the oxygen and carbon dissolution. Since it impacts the retention of O (and C) at the surface, it is an important consideration in the segregation of S to the surface. The details of the overall compositional variation of the surface with temperature for these alloys have been reported elsewhere[9-11]. The oxygen (oxide) content at the surface was about the same as for pure Ti, but, in general, the dissolution of the O and C occurred much more gradually. Further, the amounts of O and C on the alloy surface, even at 1000°C, were still quite significant and

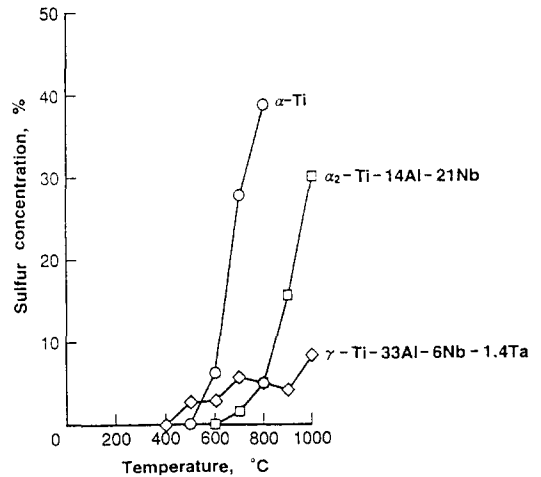


Fig. 6. Variation in S concentration for α -Ti and the α_2 and γ alloys versus temperature.

seem to be a sensitive function of the quantity of Al.

Fig. 6 shows the surface variation of S concentration as a function of temperature for α -Ti and the α_2 and γ alloys. It is interesting to note that the α_2 showed no surface S until 600°C and then monotonically increased to about 30% at 1000°C. The S comprised only about 5% on the surface of the α_2 at 800°C compared to the 40% observed on pure Ti, even though there was much more bulk S in these samples (135 wppm) than in any of the other samples studied, especially pure Ti (1.5 wppm). Simultaneous with the increase in S on the α_2 , the $Al_{L_{2,3}}VV$ signal increased and showed a peak splitting characteristic of $Al_2O_3 + Al$. This retention of the O by the Al augments the O lost by the Ti and slows down the dissolution. As the Al_2O_3 shoulder declined (as well as the Al) at 900°C and 1000°C, the S increase was proportionate and seems to mirror the decrease of surface oxygen. The γ alloy behaved quite differently in that the S began to segregate much earlier than the α_2 ($T \approx 400^\circ C$) but never increased above a surface concentration of about 8%. The low level of the S (bulk concentration 29 wppm) indicates that

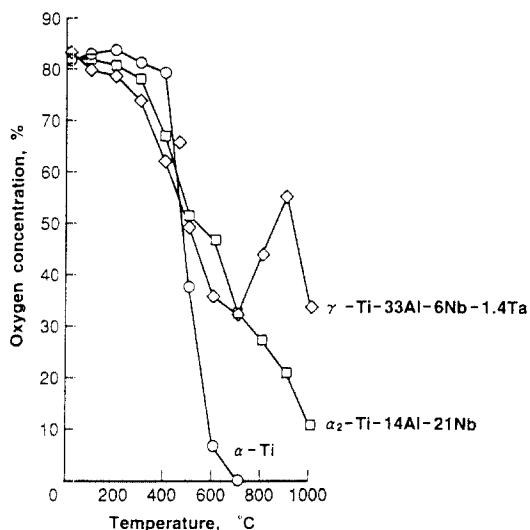


Fig. 7. Variation in O concentration for α -Ti and the α_2 and γ alloys versus temperature.

the O in the growth of the Al₂O₃ inhibited the S segregation. Eventually, the O dissociated between 900°C and 1000°C and dissolved into the bulk, allowing the S to make a final signal upturn in surface concentration. The Al at 1000°C appears to be characteristic of the metal in solid solution.

Fig. 7 represents the α -Ti and the α_2 and γ alloys with their respective O dissolution curves superimposed. The mirror imaging of O and S intensities clearly suggests that the segregation of S is a sensitive function of the surface coverage of oxygen. Although C behaves somewhat similar to that of O, it is not clear what its effect is on the S segregation. The segregation rate data for the Ti-aluminides were not measured because of the dynamic variations of the surface composition inhibiting the segregation process.

4.3. Desulfurization of α -Ti

The removal of the S from the Ti (and from all the alloys) was accomplished by either simultaneous heating and sputtering or by exposure to a high pressure of hydrogen or oxygen. Fig. 8 shows the decrease in the S signal as a function of

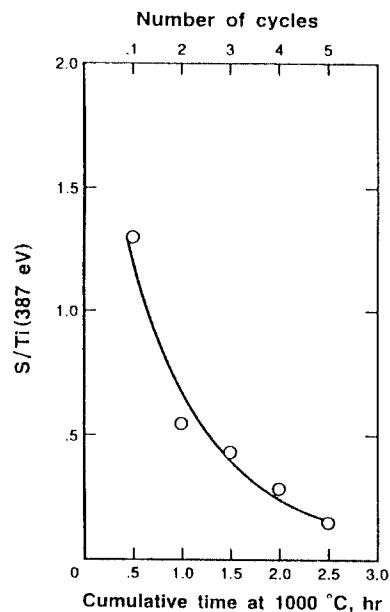


Fig. 8. Variation of S Auger peaks versus number of cycles (heating and sputtering).

the number of cycles. The variation of the S normalized to the Ti(387 eV) transition is shown as a function of the number of cycles after the surface sulfur was maximized by heating at 800°C for 2 h. The elevated temperature of 600°C during sputtering was required because the segregation rate must be sufficiently high to deplete the bulk of S and to ensure that no adsorbed C or O (they dissolve at this temperature) from the gas phase would impede the segregation. Coad and Riviere in a previous work observed that a temperature of 780°C was necessary to completely remove the S and obtain a clean surface because the Ti was continuously adsorbing the C and O from the residual gases[6]. The α_2 alloy was also depleted of S both by heating and sputtering. This alloy seems to segregate much less S than the pure Ti even though it contained a factor of 90 greater bulk S concentration. The γ alloy was never completely free of the oxygen, so very little S segregated to the surface, thus making the S bulk depletion very slow in this temperature range. We may expect

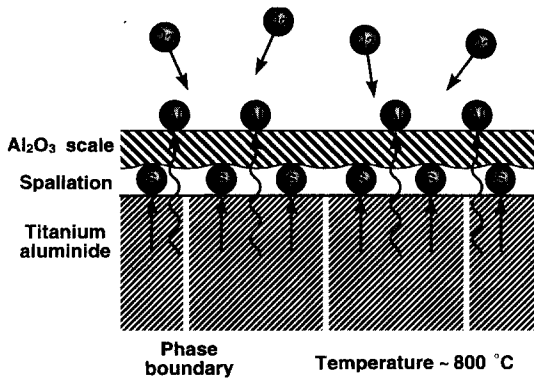


Fig. 9. Al segregation to surface forms Al_2O_3 scale. Sulfur segregation to interface creates spalling.

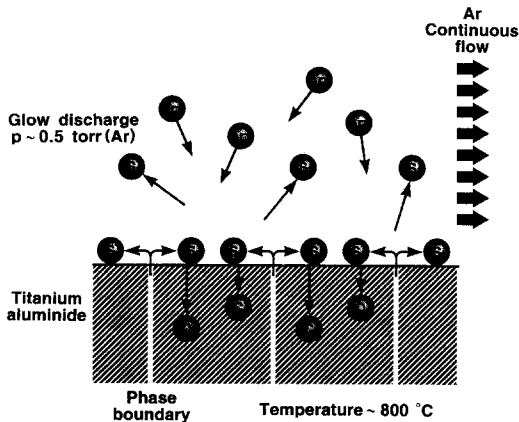


Fig. 10. A model of the desulfurization in Ti. Surface carbon and oxygen dissolve into bulk of alloy. Later sulfur segregates to surface and is removed by Ar⁺ ion sputtering.

that in case of the Al_2O_3 coated on the Ti surface, Al_2O_3 scale spallation can be occurred due to sulfur segregation and weakening at the Al_2O_3 -Ti interface as shown in Fig. 9.

We may suggest a model of the desulfurization in Ti and T-aluminide alloys as shown in Fig. 10.

5. Conclusions

It is clear from this study that the intensity of the Ti(418 eV) Auger peak is not affected by the amount of surface segregated sulfur from the bulk,

but only affected by the amount of surface oxygen and carbon. This indicates that the segregated sulfur on titanium is not forming sulfide and is weakly bound.

The activation energy for S segregation in polycrystalline Ti was determined to be 16.7 kcal/mol which is lower than reported for single-crystal Ti(0001). This indicates a strong grain boundary component in the overall transport.

Carbon and oxygen appear to completely dissolve (as detectable by AES) into the bulk of pure Ti at temperatures greater than 400°C. However, in titanium aluminide alloys, the species are never completely removed, even after heating to 1000°C.

At elevated temperatures (700-1000°C), the Ti-aluminide alloys (α and γ), show the presence of surface Al, which enhances the retention of surface oxygen and proportionally reduces the S segregation.

The dissolution of surface oxygen with temperature is a mirror image of the S segregation, indicating that S will only segregate when the oxygen leaves available surface sites.

Acknowledgements

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