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RESEARCH ARTICLE

Constant Values Predicted by Theory to Determine the Transition Intervals between Stress-Induced Martensite and Gum Metal in Ti-based Alloys

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ABSTRACT

Designing a new alloy requires an understanding of how the components mix to generate distinct properties, and then applying that understanding to create new functionalities or drastically improve current ones. This study investigates the connection between the electron-to-atom ratio (e/a), bond order (Bo), and bond degeneracy (Md) and transformation-induced super elasticity in Ti alloys. A more complete picture of the relationship between the "Magic Numbers" and phase stability, elastic, and super-elastic behavior in Ti-alloys may be seen when all three are considered. Such a comprehension could significantly influence the development of Ti alloys with improved mechanical properties.

Keywords: *Constant Values; Transition Intervals; Stress-Induced Martensite; Gum Metal; Ti-based Alloys*

Introduction

The primary objective of the metallurgist has been to develop the imagination and skill necessary to precisely tune the physical and structural qualities of materials to meet specific requirements. In this sense, comparatively, properties will be closely related to the concentration of elements in the system. The observation by Hume Rothery, Bradley, West-green and co-workers earlier that noble metal alloys are mainly a function of electron per atom ratio (e/a), has been one of the most celebrated empirical rules of metallurgy (Hume-Rothery, 1926; Sivertson, Nicholson, 1967). The question of lattice stability plays an important role in any discussion of the physics of pure metal or alloy system. This is particularly true of Ti alloys, whose lattice stability (i.e., structural phase stability) has technical as well as fundamental significance. The crystal structures of the three long periods of transition elements change more or less systematically from hcp through bcc to fcc as their group numbers increase from IV to VIII. According to Barrett and Massalski. (1980), the use of e/a rather than atomic or weight percent composition as a parameter against which properties are compared almost never fails to bring about interesting correlations when applied to elemental data. Empirical studies have shown that in many alloy systems the electron concentration is the important parameter that influences such factors as the extent of primary solid solubility, the presence or absence of a particular structure, the range and stability of intermediate phases, the formation of long–period superlattices, trends in lattice spacings, the number of vacant sites in defect structures, the stacking fault energy, and many others (Barrett, Massalski, 1980). In calculating the e/a ratio, valences are assigned to elements and based on that, the maximum solubility of many elements in Cu and Ag were calculated corresponding to an e/a ratio of 1.35-1.4. These limits correspond closely to concentration at which the Fermi–sphere approaches the first Brillouin zone. Also, from an energetic point of view, Oriani et al (1936), working on energy of transformation in Au and Cu alloys stated further that all changes in the energy of alloy system owe their origin to the electronic considerations. The change in energy of metals upon alloying can be attributed to the change in electronic energy or the misfit or strain energy.

To explain the correlations observed in many alloy composition ranges, it is therefore of critical importance to demonstrate the contribution of this electron per atom (e/a) ratio in controlling the mechanical properties, the stability of solid solutions and phase constituents. In this work, we are reporting a calculative theoretical analysis based on data from literatures on the major role of e/a, where the magnitude of this parameter can play an important part in determine more clearly the intervals for α, β, α+β phase(s) stability, Stress Induced Martensite formation and Gum metals in Ti based alloys. The patterns that emerge as the magnitude of e/a is plotted against Bond order (Bo), Molecular orbital number (Md) and Activation energy (eV) are sufficiently precise in recognizing the role of e/a. The relationship could be very valuable in the design and applications of Ti alloys.

Determination of the α and β Phase Correlations in Ti Alloys

In this formulation, we propose a new averaging approach by modifying the Morinaga, Yukawa, Maya, Sone and Adaki (1988), design of Ti alloys. The present formulation, on the other, propose a pair of three matrix averages in the design of Ti alloy by comparing the Bond order (Bo) and Molecular orbital (Md) with the compositional average valence electron number (e/a).

The estimate is clearer and compares better with experimental data to show the suitability of the method in predicting the stability of α and /or β phase in Ti alloys. Its applicability in predicting the stability of stress induced martensite (SIM) and Gummetals behaviours in Ti alloy is also apparent. The value of (e/a) is obtained according to the following eqn.3.1 by Wagner, Otooni, Krakow and Ottoni, (1998).

$$\boldsymbol{e/a} = \frac{\sum_{\boldsymbol{N_i}}[\boldsymbol{at}.\% \times (\boldsymbol{s}+\boldsymbol{d})_{\boldsymbol{n}} + ..\boldsymbol{N_i}}{\sum_{\boldsymbol{N}}[\boldsymbol{at}\%\boldsymbol{n} + \cdots \boldsymbol{N_i}].} \tag{1}$$

at. % =s the atomic percentage of the individual elements and

$(s+d)_n$ = the number of (s+d) electrons orbital values contributed by the metal atoms, depicted as e/a, that is specific for the alloy composition.

Metal d-orbital energy level (Md) = is the parameter which correlates with the electronegativity and metallic radius of alloying elements.

Bond order (Bo) = which is a measure of the covalent bond strength between Ti and an alloying based on the DV-Xα cluster method calculations.

The magnitudes for the constituent elements are obtained by the compositional average given by eqn.2 and 3 respectively (Wagner, Otooni, Krakow, Ottoni, 1998)..

$$\overline{Bo} = \sum_{i=1}^{n} x_i \, (Bo) \qquad (2)$$

$$\overline{\mathrm{Md}} = \sum_{i=1}^{n} \chi_i \, (Md)_i \qquad (3)$$

In verifying the suitability of the formulation in determining the stability limits for α or β phase stability, Figs.1-4 have been displayed to illustrate the results of the calculation by using the three parameters to shows the representation for the α and β phases respectively, based on data from experimentally verified alloy compositions of commercial α and β Ti alloys (See Tables 1-3).

Table 1: Valence, Bo, Md and the atomic number of elements used in this study

Elements	*Ti*	*V*	*Cr*	*Mn*		*Fe*	*Co*	*Ni*	*Cu*	*Al*	*Zr*	*Nb*	*Mo*	*Hf*	*Ta*	*W*	*Si*	*Sn*
S+d	4	5	6	7	8	9	11	12	3	4	5	6	11	5	6	4	4	
Md(ev)	2.447	1.672	1.478	1.194	0.97	0.807	0.724	0.567	2.2	2.934	2.424	1.96	2.98	2.53	2.072	2.2	2.1	
Bo-β	2.79	2.805	2.779	2.723	2.65	2.529	2.412	2.114	2.426	3.086	3.099	3.063	3.11	3.114	3.13	2.56	2.28	
At. no	47.87	50.94	51.97	54.93	55.8	58.93	58.69	63.55	26.98	91.22	92.9	95.94	178.5	180.9	183.8	28.09	118.7	

Table 2: β-alloys studied (wt. % and at. %) and their e/a, Bo and Md values

S/n	*α-Ti alloys (wt. %)*	*α-Ti alloys (at. %)*	*(e/a)*	*Md*	*Bo*
1	Ti-3Al-4V	Ti-5Al-3.7V	3.986	2.408	2.766
2	Ti-6.3Al-1Sn-1Zr-3.3Mo-0.18Si	Ti-10.9Al-0.39Sn-0.51Zr-1.6Mo-0.3Si	3.923	2.411	2.752
3	Ti-5Al-3Mo-1V	Ti-8.7Al-1.5Mo-0.9V	3.952	2.414	2.747
4	Ti-6Al-1.7Fe-0.1Si	Ti-10.18Al-1.39Fe-0.16Si	3.954	2.400	2.750
5	Ti-5Al	Ti-8.54Al	3.914	2.425	2.758
6	Ti-5Al-2.5V	Ti-8.55Al-2.26V	3.937	2.412	2.759
7	Ti-4l-2V	Ti-6.8Al-1.8V	3.949	2.417	2.762
8	Ti-6Al-2Nb-1Ta-0.8Mo	Ti-10.3Al-1Nb-0.25Ta-0.39Mo	3.916	2.419	2.756
9	Ti-6Al-6Zr-0.5Mo-0.2Si	Ti-10.4Al-2.6Zr-0.24Mo-0.42Si	3.900	2.418	2.760
10	Ti-8Al-1Mo-1V	Ti-13.4Al-0.47Mo-0.89V	3.884	2.405	2.741

Table.3: β-alloys Studied (wt. % and at. %) and their e/a, Bo and Md Values

S/n	*β-Ti alloys (wt. %)*	*β-Ti alloys (at. %)*	*(e/a)*	*Md*	*Bo*
11	Ti-11.5V-2Al-2Sn-11Zr	Ti-11.4V-3.8Al-0.85Sn-6.1Zr	4.076	2.398	2.791
12	Ti-12V-2.5Al-2Sn-6Zr	Ti-11.6V-4.6Al-0.83Sn-3.2Zr	4.068	2.378	2.776
13	Ti-16V-2.5Al	Ti-14.9V-4.4Al	4.104	2.350	2.776
14	Ti-11.5Mo-6Zr-4.5Sn	Ti-6.5Mo-3.5Zr-2Sn	4.132	2.385	2.773
15	Ti-10V-2Fe-3Al	Ti-9.26V-1.69Fe-5.2Al	4.108	2.354	2.771
16	Ti-10Mo-8V-1Fe-3.5Al	Ti-5.1Mo-0.96V-0.9Fe-6.4Al	4.089	2.344	2.776
17	Ti-8Mo-8V-2Fe-3Al	Ti-4.1Mo-7.7V-1.8Fe-5.5Al	4.175	2.344	2.782

18	Ti-10V-7Mo-2Fe-1Zr-4Al	Ti-9.6V-3.6Mo-1.7Fe-7.2Al	4.163	2.317	2.755
19	Ti-6V-6.2Mo-5.7Fe-3Al	Ti-5.7V-3.1Mo-5Fe-5.4Al	4.265	2.310	2.771
20	Ti-8V-5Fe-1Al	Ti-7.54V-4.3Fe-1.8Al	4.028	2.334	2.777

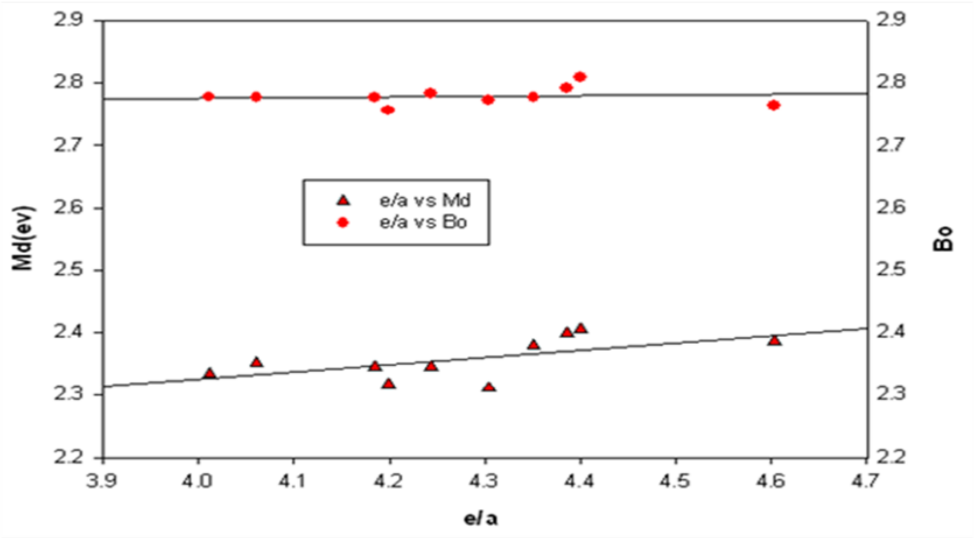

Fig.1: map showing the positions for β alloys based on e/a, Bo and Md. parameters

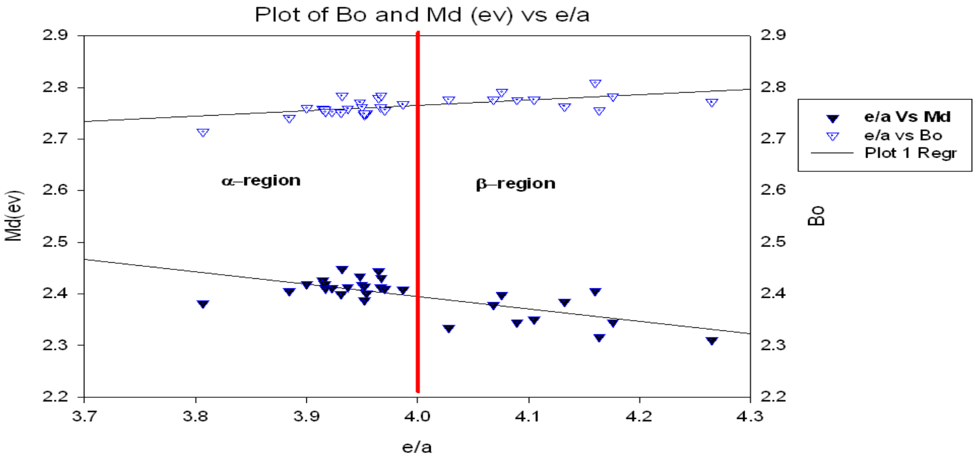

Fig. 2: map showing the areas occupied by α alloys based on e/a, Bo and Md. parameters

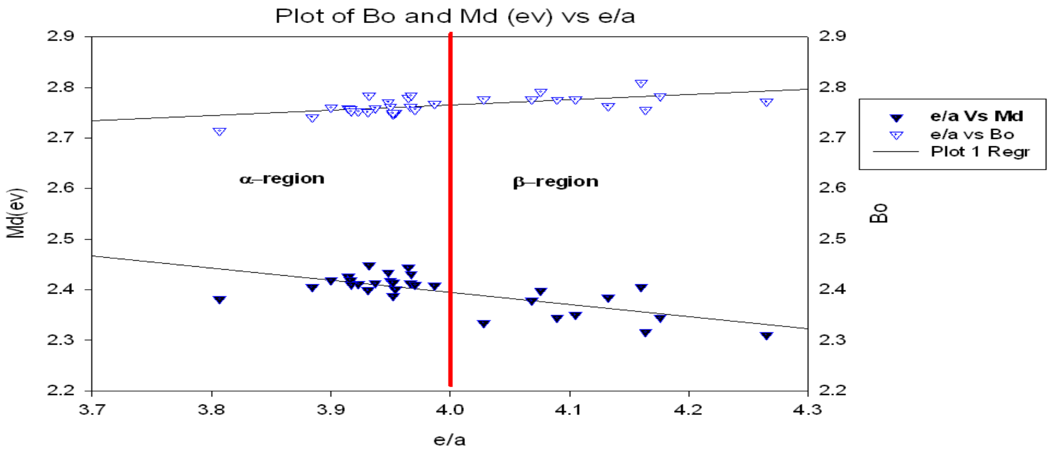

Fig.3: the positions for α and β phases based on e/a, Bo and Md. parameters

Stability of β or α Phase in a Ti Alloy

In order to predict accurately the stability of the phases, a zoning map of the regions where each of the phases are sitting is plot and shown as Fig. 4. The criteria used shows that α or β Ti alloy should be stable, if the magnitude of e/a, Md and Bo are below 4.00 and 2.40 eυ and 2.78 or a stable β phase when e/a, Md and Bo are above 4.10, 2.45eυ and 2.78 respectively has been clearly shown in this plot.

The addition of the stabilizing elements of either phase to the Ti-based alloys shifted the phase boundary and as with the compositional average of the three parameters. This is also in agreement with the requirement as put forward in Jones, (1937) and Idem, (1934) that the change in internal energy makes a predominant contribution to the free energy. However, an estimate of the volume fractions of these phases or for values in between is yet to be verified.

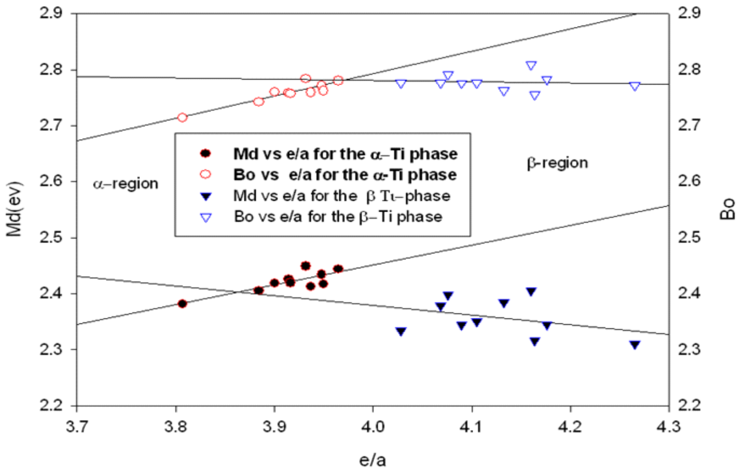

Fig.4: map showing a clear distinction for the stability of α and β phases based on the correlation of e/a, Bo and Md.

A ternary plot (Fig. 5) of e/a, Bo and Md for the two phases in the Ti alloys studied, also showed that they occupied various position. The distinction in the positions shows clearly that this correlation is better, sufficient and could be valuable in the design and application of Ti alloys. Furthermore, we can observe from the analyses that there are no significant differences in the values of bond orders for α and β in Ti based alloys. Their values are so close and very similar and may appear confusing. The same thing applies to the magnitude of Md, which has similar values as the SIM /Gunmetal alloys. On the other hand, their (e/a) values are easily observed, as a result the new model relied very much on it.

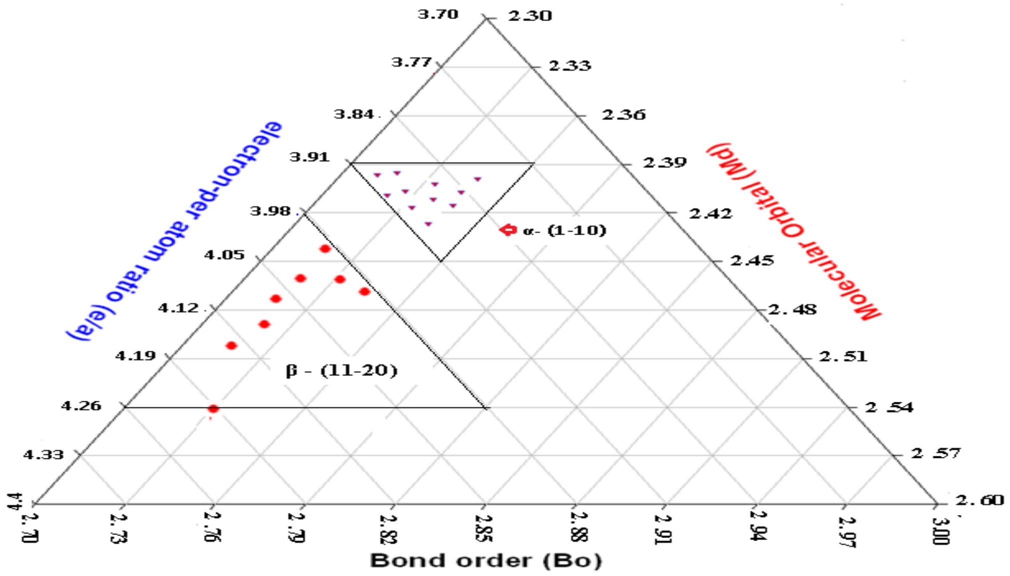

Fig.5: Ternary plot showing the distinction for the stable positions of α and β phases based on the correlation of e/a, Bo and Md. Parameters.

Estimate of the e/a Transition Interval for SIM and Gummetal Behaviors in Ti Alloy

The electron to atom ratio interval (e/a) corresponding to the transition from β to orthorhombic α" martensite phase has been determined based on the regression plot of (e/a) and the Bo and Md parameters, for several multiple element β-Ti alloys (Fig.6-9).

We have extended the present formulation to predicting the possible martensitic phase transitions (**i.e.,** stability SIM and Gummetal alloys) using some known commercial β-Ti alloys that can have such properties. From table 4 and 5, it is also apparent that the values of e/a, Md and Bo up to 4.15, 2.43ev and 2.8 might be the required limits for most multinary β-Ti alloys to display a possible martensitic phase transition. This range or relationship will therefore change by the addition of the stabilizing elements of either phase to the Ti-based alloys by shifting the phase field boundary as well as compositional average. Similarly, this was also shown with a ternary diagram for the three parameters for the Stress induced alloys (SIM) and the superplastic behaviour alloys (Gum metals) (Figs. 6 and 7).

From this ternary plot and the 3d map SIM alloys occupy a smaller region distinct region as a subset within the broader area occupied by the Gum metals alloys. The trend is quite true because SIM alloys could show super plasticity behaviour during deformation, if the applied stress or pressure is large enough for the alloy to transit from elastic deformation by twinning to plastic deformation through dislocation slip.

One can also infer that because of the good agreement with the three parameters, the stability of alloys or phases at various temperature regimes can be predictable without trials by extrapolating the value of (e/a) in eqn. 4 in Morinaga, Yukawa, Maya, Sone and Adaki (1988).

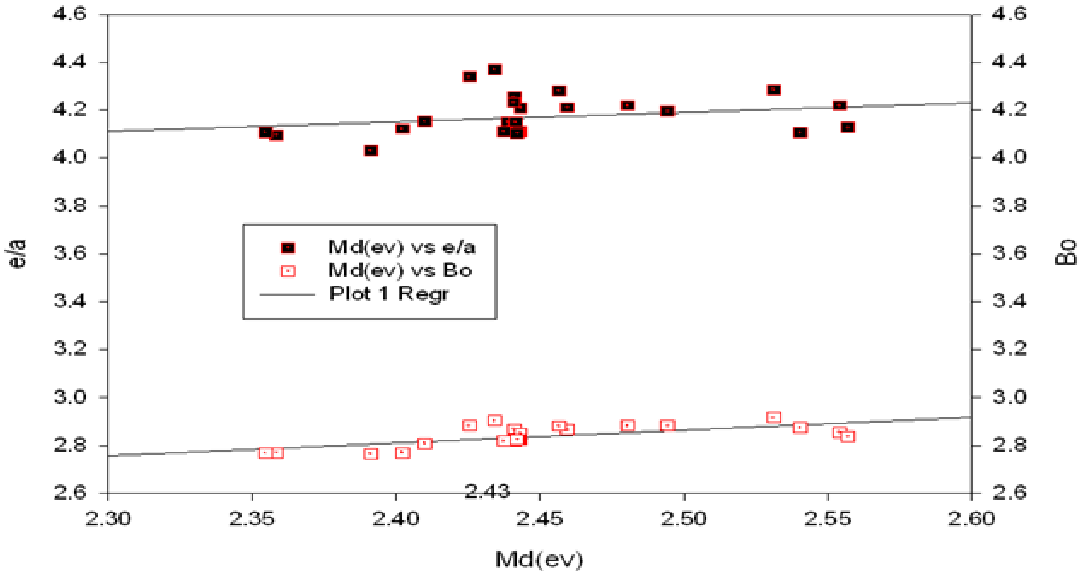

Fig. 6: Map showing 2.43 as the limiting value for alloys to possess SIM /Gunmetal behaviors in Ti alloys based on data from table 4.

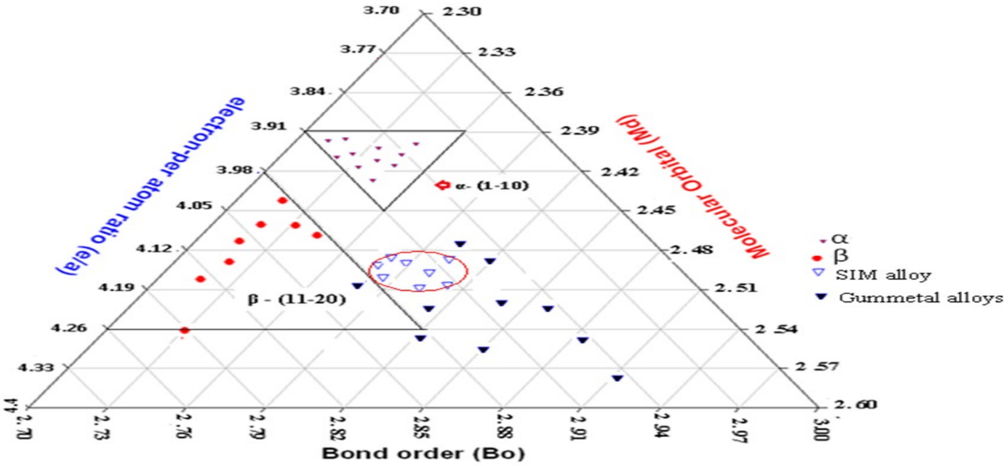

Fig. 7: Ternary map displaying the position occupied by Ti alloy that show SIM and Gum metals characteristics based on the data in Tables 5 and 6

Table 4: Names and values of e/a, Bo, Md and act. Energy for the Gummetals studied

S/n	*Gum metal-alloys*	*(e/a)*	*Md*	*Bo*	*act.En*
1	Ti-33.37Nb-11.91Zr (wt. %)	4.37	2.553	2.903	37.89
2	Ti-36Nb-2Ta-32Zr-0.3O (at. %)	4.38	2.531	2.915	38.13
3	Ti-23Nb-6.7Ta-2Zr-12O (at. %)	4.283	2.556	2.836	36.57
4	Ti-35Nb-10Ta-4.6Zr-0.16O (at. %)	4.279	2.456	2.88	37.44
5	Ti-12Ta-9Nb-3V-6Zr-1.5O (at. %)	4.24	2.402	2.769	35.26

Table 5: Names and Values of e/a, Bo, Md and Act. Energy for the **SIM alloys studied**

S/n	*Gum metal-alloys*	*(e/a)*	*Md*	*Bo*	*act.En*
1	Ti-33.37Nb-11.91Zr (wt. %)	4.37	2.553	2.903	37.89
2	Ti-36Nb-2Ta-32Zr-0.3O (at. %)	4.38	2.531	2.915	38.13
3	Ti-23Nb-6.7Ta-2Zr-12O (at. %)	4.283	2.556	2.836	36.57
4	Ti-35Nb-10Ta-4.6Zr-0.16O (at. %)	4.279	2.456	2.88	37.44
5	Ti-12Ta-9Nb-3V-6Zr-1.5O (at. %)	4.24	2.402	2.769	35.26

Activation Energy Intervals for Phase Transition in Ti Alloys

According to Mott and Jones, (1936), the change in energy of a metal upon alloying can be attributed to the change in electronic energy. This change is a form of barrier, which an alloy is expected to overcome before transitions from one phase to the other and vice versa- the activation energy. A relationship as shown by Morinaga, Yukawa, Maya, Sone and Adaki, (1988), described the vacancy formation energy in metals (E_v) related to the Fermi energy $\boldsymbol{E_f}$ by the equation:

$$\mathbf{E_v = k_i Z E_f} \qquad (5)$$

Where:
Z is the valence of the metals, which are in this case, taken as e/a ratio,
K is a numerical constant between Fermi energy. It was earlier shown (Tiwari, Hoshino, Ijima, Hirano, 1980), that E_v can be expressed in terms of the e/a ratio as the only factor influencing the activation of an alloy. A correlation based on the data from tables 4 and 5 (Fig. 9), shows the distinction based the activation energies of the phases.

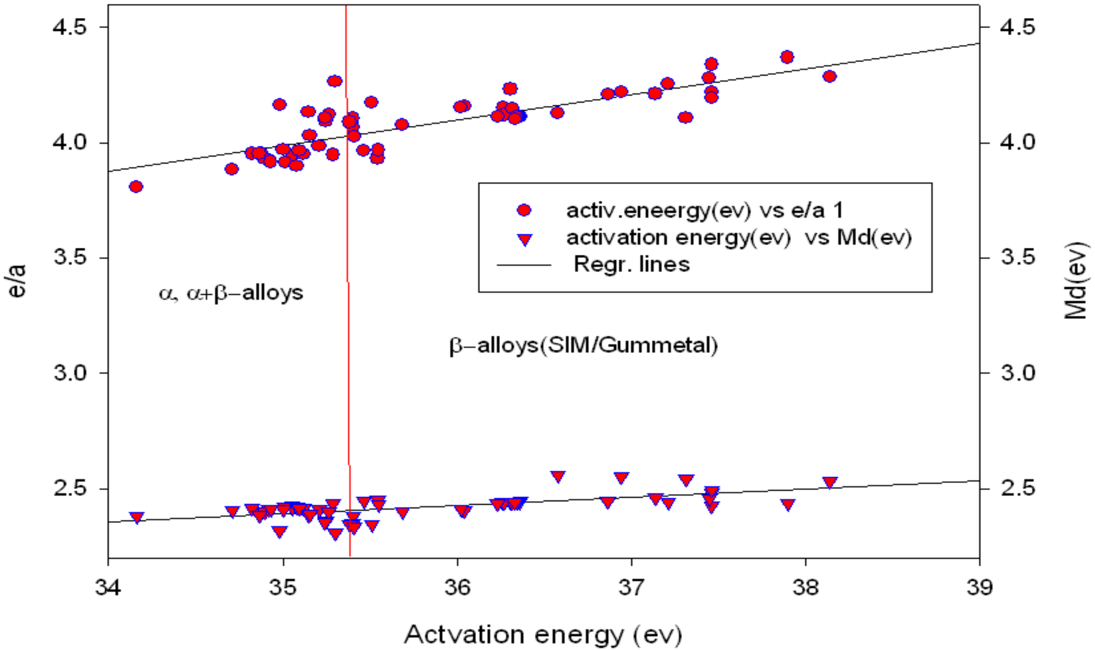

Fig.9: Plot of activation energy with e/a and Md for α, and β Ti alloys (Gummetals) based on data from tables 2-5

Conclusion

i. The objective of the calculation is to verify, if any relationship exist between e/a, Bo and Md in Ti alloys. Based on the correlations, a new method is found which can be used to design Ti based alloys. The method and plots depict clearly and sufficiently a better understanding of phase stability, elasticity and superplasiticity behaviours observed in most β Ti-alloys. The relationship found could be very valuable in the design and applications of Ti alloys
ii. The plot is better and could replay the former two parameter models because their values are so close for the two phases. That might appear confusing. The same thing applies to the Md values, which has similar values for α and most multinary β-Ti alloys. On the other hand, their (e/a) values are easily observed, as a result the new model relied very much on it.
iii. We can also infer that because of the good agreement with the three parameters, the stability of alloys or phases at various temperature regimes can be predictable without trials by extrapolating the value of (e/a) in eqn. 4
iv. A calculation based on the e/a, Md and the activation energy for α and β alloys shows that there is a demarcation. It might helpful in understanding better the deformation processes.

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