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THE SIGNIFICANCE OF A CORRELATION OF BLISTER DIAMETER WITH SKIN THICKNESS FOR Ni AND Be FOR BLISTERING MODELS

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The significance of a correlation of blister diameter with skin thickness for Ni and Be for blistering models

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ABSTRACT

It has been suggested that large lateral stresses introduced in an ion implanted surface layer may cause elastic instability and buckling of the implant layer (blister formation), and result in a relationship $D_{mp} \propto t^{3/2}$ between the most probable blister diameter D_{mp} and the blister skin thickness, t, for metals such as Be, V, stainless steel, Nb and Mo. To test this relationship a systematic study of the correlation between blister diameter and skin thickness for helium blistering of annealed polycrystalline Ni and Be has been conducted for helium ion energies in the range of 15-300 keV. For beryllium the relationship between D_{mp} (μm) and t(μm) can be fitted by the expression $D_{mp} = 24.6t^{1.25}$ whereas for nickel a best fit is obtained for the expression $D_{mp} = 1.24t^{1.15}$. These results, together with our earlier results for Nb and V show that the relationship between D_{mp} and t is strongly dependent on the type of metal studied and do not support the lateral stress model for blister formation.

Introduction

The models for blister formation in metals fall into two basic categories. One is the gas pressure model [1-9] in which the buildup of excess gas pressure in the implant region of maximum gas concentration is the main driving force for the surface deformation leading to blister appearance. The other is the integrated lateral stress model [10-12] in which it is suggested that the large lateral stresses introduced in the implanted layer leads to elastic instability and buckling of the implanted surface layer above the weakened interface region and thus gas pressure is not the driving force behind the surface deformation. The proponents of the stress model [10,12] have criticized the gas pressure model on the basis that (i) it cannot explain the relationship $D_{mp} \propto t^{3/2}$ between the most probable blister diameter D_{mp} and blister skin thickness, t, suggested for metals such as Be, V, stainless steel, Nb and Mo, (ii) for low ion energies (e.g. < 15 keV for He^+ irradiation of Nb) the blister skin thickness is larger than the projected range, and (iii) only a small fraction of the total implanted helium is actually emitted during blistering. Recently, Evans [13] has proposed an interbubble fracture mechanism of blister formation which offers an explanation for the criticisms (ii) and (iii) listed above. He questioned whether a general relation between D_{mp} and t can be applied on a sound physical basis, since the blister diameter in a given sample has been observed to vary widely [14]. The authors have shown recently [15-17] that for the case of $^4He^+$ irradiation of the two bcc refractory metals Nb and V, the $D_{mp} \propto t^{3/2}$ relationship does not hold. Furthermore, the relationship was also found to be dependent on target temperature [17]. For example, for annealed polycrystalline niobium the relationship for room temperature irradiation was $D_{mp} = 10.3\ t^{1.22}$, whereas for irradiation at 700°C it was $D_{mp} = 5.3\ t^{1.05}$, an almost linear relationship between D_{mp} and t. According to the stress model, the value of the exponent should be temperature independent. The aim of the present work was to see how the D_{mp} - t relationship changes for an fcc metal, nickel, and an hcp metal, Be. For Be, EerNisse and Picraux [10] suggested a $D \propto t^{3/2}$ relationship, but there was only one data point on the plot of D_{mp} vs. t. To the author's knowledge, there is no data available on the D-t relationship for Ni.

Experimental procedures

Polycrystalline nickel foils of 99.995% purity (Marz grade) were obtained from Materials Research Corporation, New York. The polycrystalline beryllium foils obtained from Kawecki Berylco Industries, Inc., Hazelton, Pennsylvania were hot-rolled from a vacuum-cast ingot. The foils were first metallographically polished and then annealed for 2 h. (at 650°C for Be and at 900°C for Ni) in a vacuum of $\sim 1 \times 10^{-7}$ torr. The beryllium foils were electropolished in an electrolyte containing 100 ml phosphoric acid, 30 ml glycerol, 30 ml ethanol and 30 ml sulphuric acid at an applied voltage of 35 volts, whereas the nickel foils were electropolished in a solution of 60% glycerol and 40% phosphoric acid. The irradiations were carried out with mass analyzed $^4He^+$ ions either from a low energy d.c. accelerator (for energies < 100 keV) or from a 2-MeV Van de Graaff accelerator (for energies ≥ 100 keV) and the ion beam was incident parallel to the surface normal. During the irradiation the targets were kept at room temperature and the ion flux was kept low (5×10^{13} - 1×10^{14} ions/cm^2-sec) to minimize surface heating. The total dose for each irradiation was chosen so as to avoid blister coalescence for $^4He^+$ ion energies greater than 40 keV and minimize sputtering of blister skin for energies < 20 keV. The irradiated surfaces were examined in a Cambridge stereoscan S4-10 scanning electron microscope, and a large number of micrographs were taken for each irradiation in order to have sufficient statistics.

The size distribution of blister diameters were measured from the micrographs with the aid of a Zeiss particle size analyzer. The blister skin thicknesses were measured from ruptured edges of blister skins.

Results

Figures 1(a) and 1(b) show plots of p :jected ranges of $^4He^+$ ions in Ni and Be, respectively, for different energies. The solid curves in Figure 1 show projected ranges for $^4He^+$ on nickel and for beryllium, respectively, for different energies calculated according to Brice [18] which uses Thomas-Fermi nuclear stopping cross sections together with semiempirical values for electronic stopping powers. The dotted curves in Figure 1 were taken from the recent calculations published by Ziegler [19].

The blister skin thickness values for nickel irradiated at room temperature with $^4He^+$ ions having energies ranging from 20 to 500-keV are plotted in Figure 1(a). In this case, the blister skin thickness values for energies of 80 keV and above agree within $\sim$ 10% with the calculated projected range, whereas for energies < 60 keV the values are higher than the calculated projected range. For an energy of 20 keV the blister skin thickness is almost twice the calculated projected range. This trend observed for nickel is very similar to that observed for $^4He^+$ irradiation of niobium [20].

The experimentally measured blister skin thickness values for $^4He^+$ ion irradiated Be for ion energies from 10 to 100-keV are also plotted in Figure 1(b). It may be noted that for the energy range 15- to 40-keV, the skin thickness values agree within ∿ 10% with the calculated projected range. For energies below 15 keV the skin thickness values are higher than the calculated projected range, whereas for energies of 60 keV or higher, they are lower than the projected range calculated according to Brice [18], but agree well with those calculated by Ziegler [19].

The blister diameters were analyzed from a large number of micrographs in order to obtain better statistics. Table I summarizes a typical data set for annealed polycrystalline nickel. Here, the number of blisters analyzed for each energy are listed together with the values for minimum (D_{min}), maximum (D_{max}), most probable (D_{mp}) and average (D_{av}) blister diameter. The standard deviation of the blister diameter distribution for each energy is also listed in Table I. In the last two columns the values for experimentally measured blister skin thicknesses are compared with the projected ranges calculated according to Brice [18]. For a $^4He^+$ ion energy of 500 keV, the blister skin thickness value is considered reliable while the blister diameter (e.g. D_{mp} and D_{av}) values are not considered to be reliable because one observes only a few large blisters over the entire bombarded area. energies below 20 keV we feel that there are large uncertainties in the values of D and t for reasons discussed earlier [17].

Figure 2 shows a double logarithmic plot of blister diameter vs. blister skin thickness for annealed polycrystalline nickel irradiated at room temperature with $^4He^+$ ions. The ranges of blister diameters observed at a given projectile energy, i.e., for a given mean blister skin thickness, are shown by the vertical bars and the ranges of skin thickness are shown by the horizontal bars in Figure 2. The values of most probable D_{mp} and the average blister diameter D_{av}, given in Table I are also plotted in Figure 2 for a given mean blister skin thickness. The solid line is a power relation fit of D_{mp} with mean blister skin thickness, t, and it gives the relationship

$D_{mp} = 12.4\ t^{1.15}$, where D_{mp} and t are given in units of micrometers. The curve fitting was done in the manner described earlier [17] for Nb, and the coefficient of determination r^2, which indicates the quality of the fit (a value of r^2 closer to unity indicates a better fit than a value closer to zero) for the above fit was 0.93. A power relation fit for the average diameters, as plotted in Figure 2, with the mean blister skin thickness, t, gave the relationship $D_{av} = 16.2\ t^{1.39}$ (with $r^2 = 0.96$), and for the minimum blister diameter D_{min} with t gave the relationship $D_{min} = 10.74\ t^{1.82}$ (with $r^2 = 0.94$).

Figure 3 shows a double logarithmic plot of blister diameter against skin thickness for annealed polycrystalline beryllium irradiated at room temperature with $^4He^+$ ions. Here, also, the vertical bars represent the range of blister diameters observed at a particular mean blister skin thickness, whose error limits are shown by the horizontal bars. Also plotted in Figure 3 are the values for the most probable and average blister diameters. A power curve fit of D_{mp} with t gives the relationship $D_{mp} = 24.6\ t^{1.25}$, which is shown as the solid line in Figure 3. The fit is quite good with $r^2 = 0.99$. Power curve fits for D_{av} with t and D_{min} with t, give the relationship $D_{av} = 31.6\ t^{1.4}$ (with $r^2 = 0.96$) and $D_{min} = 16.4\ t^{1.57}$ (with $r^2 = 0.88$), respectively.

Discussion

The results presented in this paper for a fcc metal, Ni and a hcp metal, Be, together with those we have reported for bcc metals, V and Nb, indicate that the relationship $D_{mp} \propto t^{3/2}$, predicted by the lateral stress model does not hold. According to the lateral stress model [10] the most probable blister diameter, D_{mp} can be written as

$$D_{mp} = \left[\frac{K \quad E}{2.5 \times 10^{-4}(1-p^2)\sigma_y}\right]^{1/2} t^{3/2} \qquad (1)$$

where E is Young's modulus, p is Poisson's ratio, σ_y is the yield strength, t is blister skin thickness and K is a geometric factor which ranges from 1.4 to 4.9 for elastic edge conditions ranging from a simply supported edge to a clamped edge, respectively. EerNisse and Picraux [10] claimed that the D-t relationship predicted by equation (1) agreed within 40% with the experimental data for Nb, V, Be, Mo, Ti, Pd and 4301 stainless steel. However, as pointed out earlier, for metals such as Be and V there were only one or two data points on which the correlation was based. For the case of Nb the authors have shown earlier [17] that the data used for the $D_{mp} \propto t^{3/2}$ correlation over a broad range of $^4He^+$ ion energies may have suffered from poor statistics for high energies (> 1 MeV) and there may be large errors in the values of D_{mp} and t for energies below 15 keV, since they depend strongly on the total dose at these low energies [17].

Table II compares our experimental D_{mp} - t relationships for Be, V, Ni and Nb with those calculated from equation (1) for the two extreme values of K using the values of E, p, and σ_y from the literature [21-23]. One should notice that these values are characteristic for annealed metals and may differ from those for irradiated metals. It can be seen that the agreement between the experiment and the predictions from the stress model is far from satisfactory. Even for the extreme case of a simply supported edge K=1.4) the pre-exponent factor in the D_{mp}-t relationship predicted by the stress model is much larger (by almost a factor of 2-4 for V, Ni, Nb) than the experimental value. Furthermore, the stress model predicts the exponent of t to be independent of material, whereas the experimental values show them to be strongly dependent on the type of metal (e.g. value of exponent varies from 0.85 for V to 1.25 for Be) studied. Recently, Van Guysse et al [24] have tried to fit their data for 21-keV He^+ ion irradiated rhenium with the relationship $D \propto t^{1.45}$, but their data were taken from blisters formed at only one energy of 21 keV with the irradiation temperature as the variable. The fitting was done for only a small range of values for t (between ∿ 0.06 - 0.12 μm). Thus, it is difficult to say if $D \propto t^{1.45}$ will indeed be valid for rhenium over a larger range of D_{mp} and t values.

The D_{mp}-t relationships determined experimentally in these studies differ significantly from those suggested by other authors [10,12] and cannot be considered as supporting evidence for a model for blister formation based on integrated lateral stress. Furthermore, it should be realized that the gas pressure model for blistering does not imply a linear relationship between D_{mp} and t, as has been discussed earlier [17]. Our earlier observation [16] that nearly spherical blisters can be formed with bases of smaller diameter than that of the blister diameter support, in certain cases, the gas pressure driven blister model. Furthermore, recent results by Evans and Eyre on thin molybdenum samples irradiated with 100 keV He^+ ions show that blisters can form on the rear surface (opposite to the implanted surface) an observation which is incompatible with the lateral stress model. A criticism of the gas pressure model that, at low ion energies the thickness of blister skin corresponds to depths larger than the projected range (see Fig. 1), an observation which was claimed to be incompatible with the gas pressure model [10,12], is not valid for the following reason: Our recent studies [26,27] on depth distribution of helium bubbles for 20-keV He^+ ion irradiation of nickel at 500°C show that the peak in the swelling due to helium bubbles or voids occurs at a depth much larger than the calculated projected range, but the peak swelling depth agrees well with the mean blister skin thickness for that energy. Thus, the observation that the blister skin thickness is larger than the projected range for low ion energies is quite consistent with the gas pressure model. In addition, Evans [13] has offered some qualitative arguments for interbubble fracture to occur at a depth larger than the peak in the helium distribution.

Another criticism raised by the proponents of the stress model, that only a small fraction of the total helium fluence is actually released during blistering is not really a valid one because experimentally, one does not always observe many cracked blisters. Unless the blisters are ruptured no large gas bursts will be seen. In those cases where severe flaking occurs, large bursts of gas release have been observed by Bauer and Thomas [28]. In the early experiments on D^+ irradiation of copper by Kaminsky[1], the number of gas bursts correlated very well with the number of ruptured blisters (pits) observed on the surface.

Conclusions

The relationship between the most probable blister diameter, D_{mp}, and the mean blister skin thickness, t, for nickel held at room temperature, can be expressed as $D_{mp} = 12.4\ t^{1.15}$, and for annealed polycrystalline beryllium, can be expressed as $D_{mp} = 24.6\ t^{1.25}$. These relationships, together with earlier results obtained for Nb and V, show that the relationship between D_{mp} and t is dependent on the type of metal studied and does not support the lateral stress model for blister formation which predicts $D \propto t^{1.5}$ for many metals, including Be, Nb and V.

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Figure Captions

Figure 1 Projected ranges of $^4He^+$ ions (a) in nickel and (b) in beryllium as a function of projectile energy. The solid curve marked "Brice" was calculated using Thomas-Fermi nuclear stopping and Brice's semi-empirical expression for electronic stopping. The dotted curve was taken from the range-energy curves calculated by Ziegler. The data points with error bars are measured skin thickness values for annealed polycrystalline metals irradiated at room temperature with $^4He^+$ ions to total doses ranging from 0.1 to 0.5 C/cm^2.

Figure 2 A double logarithmic plot of blister diameter against blister skin thickness for annealed polycrystalline nickel irradiated at room temperature with $^4He^+$ ions. The error bars show the ranges of values observed at a given $^4He^+$ ion energy.

Figure 3 A double logarithmic plot of blister diameter against blister skin thickness for annealed polycrystalline beryllium irradiated at room temperature with $^4He^+$ ions.

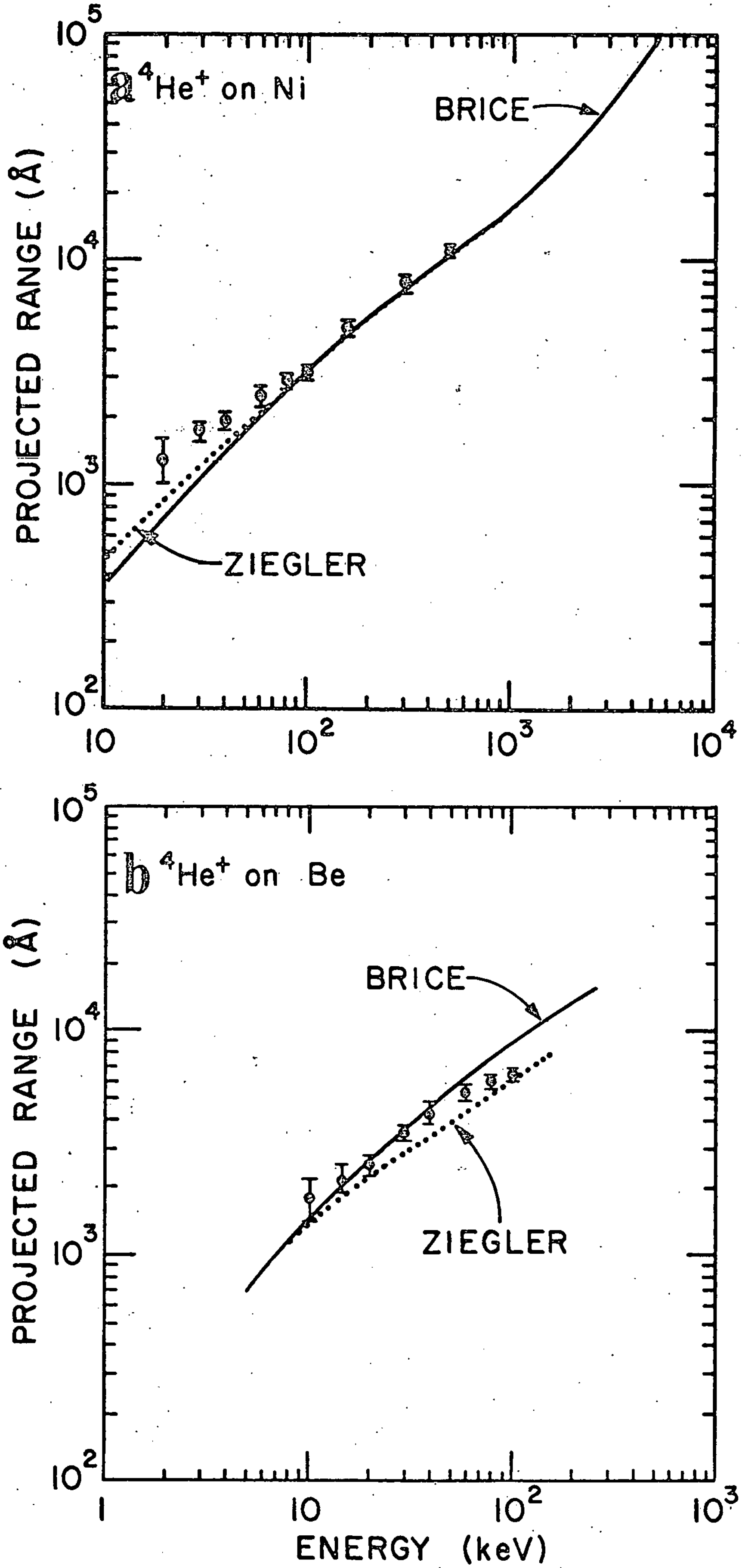
TABLE I Blister diameter and blister skin thickness for annealed polycrystalline Ni irradiated at room temperature with $^4He^+$ ions of various energies.

$^4He^+$ ion energy (keV)	No. of Blisters Counted	BLISTER DIAMETER (μm) Min. Dia, D_{min}	Max. Dia, D_{max}	Avg. Dia, D_{av}	Most Probable Dia, D_{mp}	Standard Deviation	Blister Skin Thickness, t (μm)	Projected Range Calculated According to Brice, (μm)
20	515	0.22	1.25	0.91	0.99	0.18	0.13 ± 0.03	0.0666
30	435	0.36	1.95	1.11	1.45	0.35	0.7 ± 0.02	0.1006
40	762	0.41	2.47	1.50	1.73	0.39	0.19 ± 0.02	0.1336
60	413	1.14	3.90	2.62	3.07	0.58	0.25 ± 0.03	0.1955
80	541	1.44	4.40	3.18	3.28	0.45	0.27 ± 0.02	0.2527
100	582	1.52	5.90	3.82	4.18	0.74	0.30 ± 0.02	0.3060
150	464	3.30	11.10	5.13	4.90	1.14	0.50 ± 0.04	0.4256
300	384	4.76	27.70	10.74	8.0	4.10	0.77 ± 0.1 0.06	0.7207
500	---	---	---	---	---		1.1 ± 0.05	1.0283

TABLE II Power relationships for most probable blister diameter, D_{mp} (μm) and mean blister skin thickness, t (μm) as predicted by the lateral stress model and as obtained experimentally for different metals.

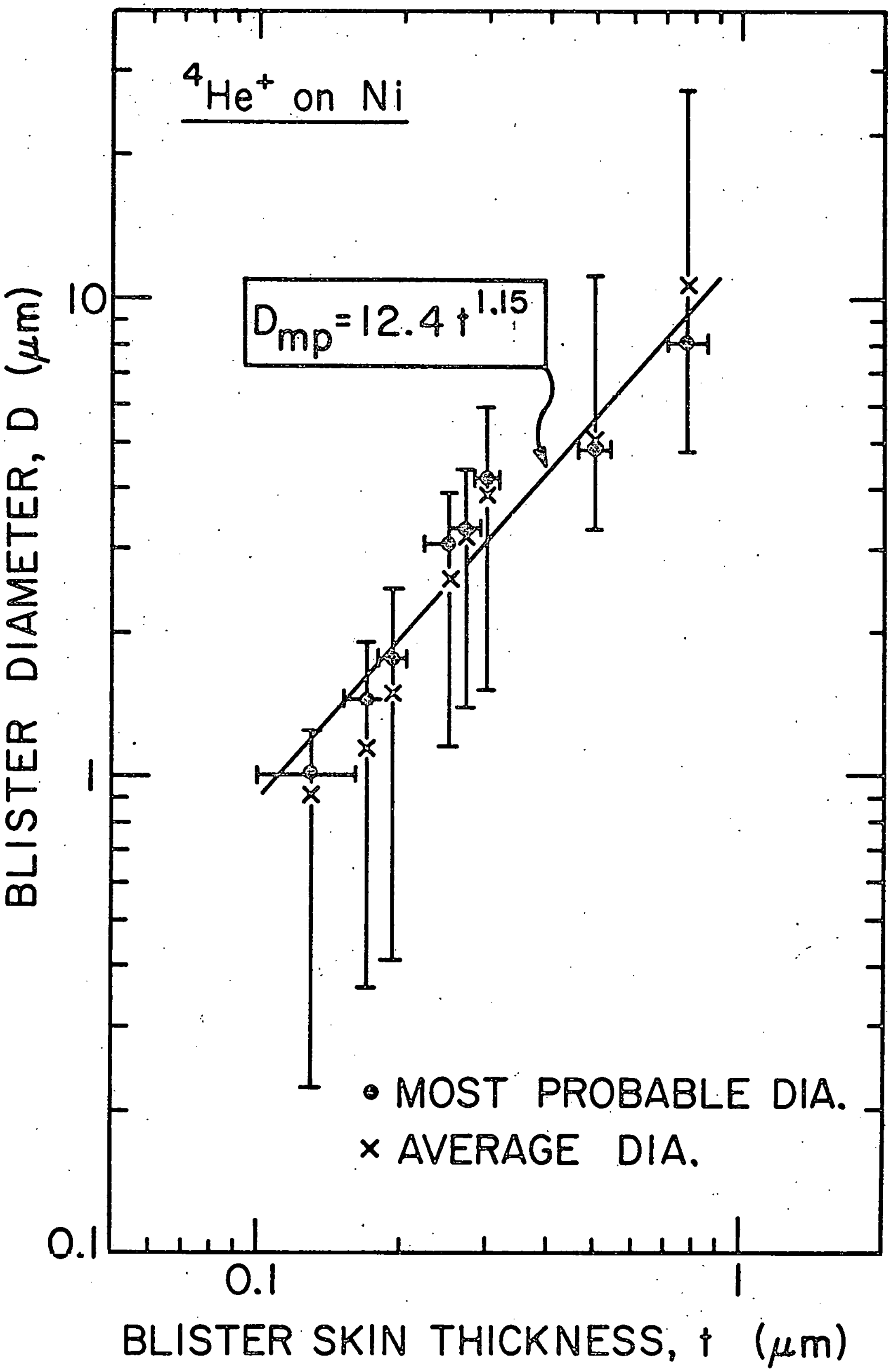
Metal (annealed polycrystalline)	Young's Modulus E ($\times 10^{12}$ dynes/cm^2)	Poisson's Ratio, p	Yield Strength σ_y ($\times 10^{9}$ dynes/cm^2)	Relationship predicted by stress model* for k = 4.9	Relationship predicted by stress model* for k = 1.4	Experimental Relationship
Be	2.75	0.027	1.18	$D_{mp} = 54.7t^{1.5}$	$D_{mp} = 29.2t^{1.5}$	$D_{mp} = 24.6t^{1.25}$
V	1.38	0.35	1.17	$D_{mp} = 51.3t^{1.5}$	$D_{mp} = 27.4t^{1.5}$	$D_{mp} = 6.3t^{0.85}$
Ni	2.06	0.276	0.58	$D_{mp} = 86.8t^{1.5}$	$D_{mp} = 46.4t^{1.5}$	$D_{mp} = 12.4t^{1.15}$
Nb	1.03	0.39	1.45	$D_{mp} = 40.0t^{1.5}$	$D_{mp} = 21.4t^{1.5}$	$D_{mp} = 10.3t^{1.22}$

*Calculated using the expression $D_{mp} = \left[\frac{K\,E}{2.5 \times 10^{-4}(1-p^2)\,\sigma_y}\right]^{1/2} t^{3/2}$ given by lateral stress model [10]



a $^4He^+$ on Ni
BRICE
ZIEGLER
PROJECTED RANGE (Å)
10^2
10^3
10^4
10^5
10
10^2
10^3
10^4
b $^4He^+$ on Be
BRICE
ZIEGLER
PROJECTED RANGE (Å)
1
10
ENERGY (keV)

FIGURE 1



$^4He^+$ on Ni
$D_{mp}=12.4\,t^{1.15}$
BLISTER DIAMETER, D (μm)
BLISTER SKIN THICKNESS, t (μm)
0.1
1
10
0.1
1
• MOST PROBABLE DIA.
× AVERAGE DIA.

FIGURE 2

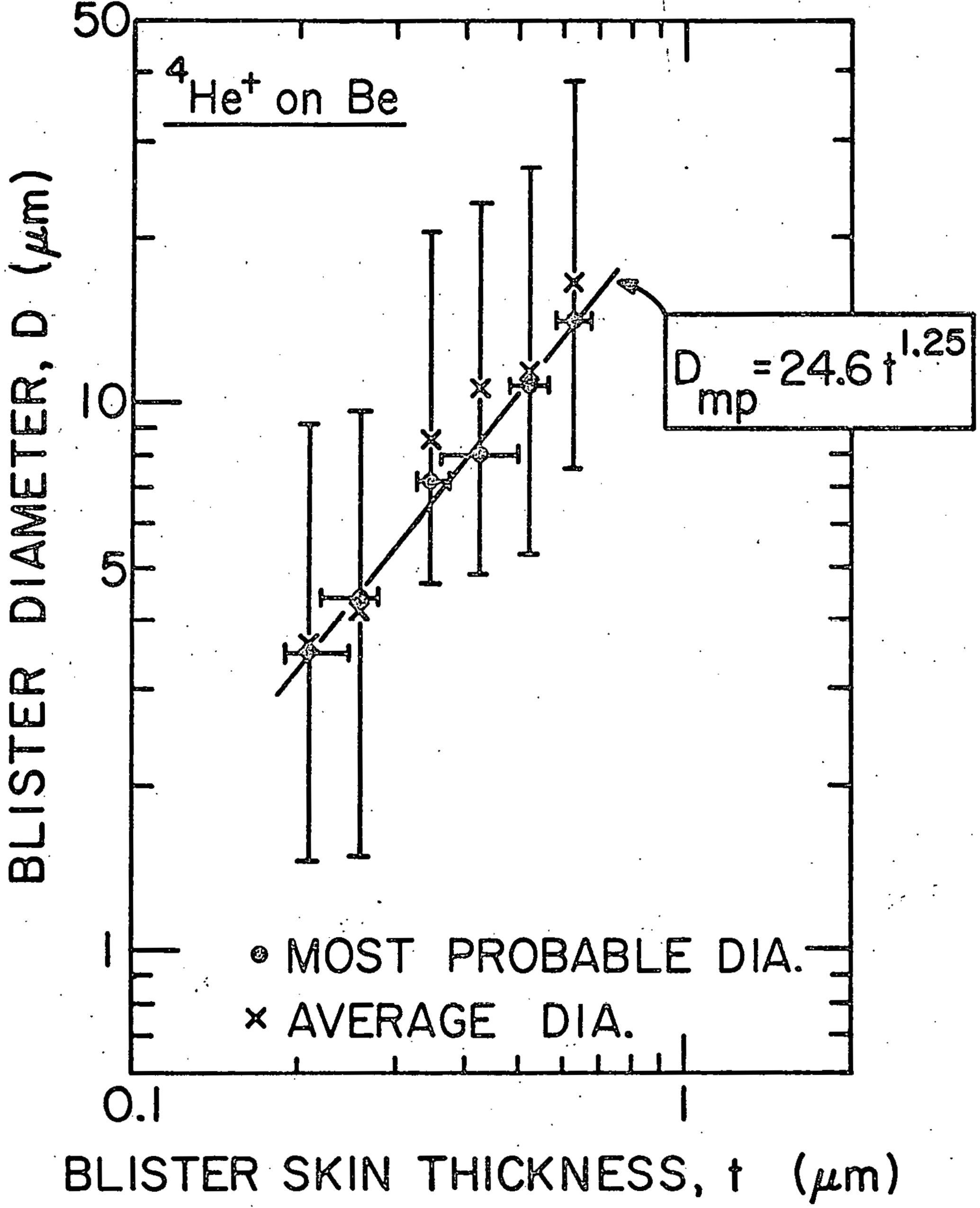

50
$^4He^+$ on Be
BLISTER DIAMETER, D (μm)
10
5
1
$D_{mp} = 24.6\,t^{1.25}$
MOST PROBABLE DIA.
AVERAGE DIA.
0.1
1
BLISTER SKIN THICKNESS, t (μm)

FIGURE 3