Enhancement of Mechanical Properties in Microlaminate Composite Materials Produced by Physical Vapor Deposition

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Abstract

The attempt to enhance the strength of materials has been an important subject for materials engineering and scientists. The strength of materials is termed as the ability to support high load without excessive deformation and without breaking catastrophically. The control of dislocation densities and barriers to the movement of dislocations have been considered to be the important methods for the strengthening materials. One of the approaches is mechanical blocking of dislocations by alternately depositing material layers. The typical structure of materials is multilayered and laminated composites. The thickness of each layer is typically in the range of nanometer. To avoid confusion with other terminology, they may be defined as microlaminate composite materials.

The manufacturing process of multilayered laminate structure will be introduced. And the current theoretical theories will be reviewed in view of strengthening of microlaminate composite materials.

I. Introduction

The attempt to produce high strength materials has been an important subject for many years. The term high strength materials includes the abilities to support high load without excessive deformation and without breaking catastrophically. The deformation mechanism of materials has been described in terms of dislocation movement by many researchers. The control of dislocation density and barriers to the movement of dislocations have been considered to be the important methods for the strengthening materials(1)(2).

One of the approaches is mechanical blocking of dislocations by alternately depositing material layers. The materials have multilayer structure and are laminated composites. The thickness of layers is typically sub-micron. In order to avoid confusion with other terminology, they may be defined as microlaminate composite materials.

Microlaminate composite materials have a significant advantage over fibrous composites as high strength and high toughness materials because of their isotropic properties in the plane of the sheet. The properties of the laminate composites depend on the structure and properties of each of the components, the respective volume fraction, the interlamellar spacing, their mutual solid solubility and the possible formation of a brittle intermetallic compound between them. Thus the structure and mechanical properties of these microlaminate composite materials can be varied and controlled by deposition condition

Numerous researchers have made microlaminate composite materials by physical vapor deposition, based on the Koehler theory(3), Hall-Petch relationship(4)(5) and supermodulus effect(6). Bunshah has made composite materials of metal/metal systems (Cu/Ni, Cu/Fe, Cr/Cu and Ti/Ni)(7)(8), metal/ceramic systems (Ni/TiC)(9) and ceramic/ceramic systems (TiC/TiB)(10) by evaporation or the ARE process. Springer has investigated the pulsed gas process (PGP) to produce the composite materials of Al/Al oxide(11), Al/Al nitride(12) and Ta/Ta carbide system(13). Koehler(3) proposed a more theoretical approach to the strengthening mechanism in microlaminate composite materials with several boundary conditions for dislocation motion. Lehoczkey[14] derived the minimum stress required for yield from Koehler theory. Lehoczkey[14][15] has investigated the Al/Cu and Al/Ag systems deposited by evaporation.

The supermodulus effect[6] is an enhancement of the elastic modulus of materials by up to 300% for compositionally modulated metallic thin films. Hilliard and coworkers[16][17] have investigated Al/Ni, Cu/Pd and Cu/Ni systems deposited by vaporization. Theoretical attempt to explain the supermodulus effect have been based primarily on either Fermi surface-Brillouin zone interaction or coherency strain phenomena.

The manufacturing process of multilayered laminate structure will be introduced. And the current theoretical theories will be reviewed in view of strengthening of microlaminate composite materials.

II. Theory

The theoretical background of this research is based on the mechanical blocking of dislocations by alternately deposited thin layers. Thus it includes Koehler's theory and the Hall-Petch relationship.

1. Koehler's theory[3]

Koehler proposed a theoretical model to design a strong laminated composite materials with high strength and low susceptibility to brittle fracture. If a specimen is prepared by epitaxial crystal growth which consists of alternate layers of crystals A and B, their properties should be such that :

(a) The elastic constants (or line energies of dislocation) should differ by as much as possible. If material A has a high line energy, dislocations prefer to be in material B (B is soft material).

(b) The thickness of A and B layers must be small. The B layer must be thin enough so that dislocation generation cannot occur inside the B layer. This requires that the b layer be of the order of 100 atomic layers thick or less. The A layer should be about same thickness.

(c) Their lattice parameters should be nearly equal in order to grow the two crystals on one another epitaxially without having large strains at the interface.

(d) Their thermal expansions should be as close as possible so that the change in temperature will not destroy the lattice fit at the interface.

(e) The bond strength between A and B atoms should be larger, i.e., of the same order as the bonding between two A atoms or between two B atoms.

The boundary conditions at the interface between two crystals are such that the displacements and the stresses are continuous across the interface. It will be assumed that a long straight screw dislocation is near parallel to one of the interface. The screw dislocation has burgers vector b and is a distance r from the interface as shown in Fig. 1. Using the isotropic elastic theory, the force per unit length between a screw dislocation in B layer and its nearest image in A layer is given by,

$$F_1 = R\mu_B b^2 / 4\pi r \tag{1}$$

where $R = (\mu_A - \mu_B)/(\mu_A + \mu_B)$

μ_A : modulus of rigidity of high elastic material

μ_B : modulus of rigidity of low elastic modulus

Similarly, the image force attributable to the other interface is,

$$F_2 = R\mu_B b^2 / 4\pi (t_B - r) \tag{2}$$

where t_B : the thickness of B layer. The total image force acting on the dislocation as a result of its nearest images in A is thus,

$$F_t = F_1 + F_2 = (R\mu_B b^2 / 4\pi)(t_B - 2r)/[r(t_B - r)] \quad (3)$$

Because $\mu_A > \mu_B$ and $t_B > 2r$, F_t is always positive, and the dislocation is repelled from the nearest interface. The resolved shearing stress required to drive the dislocation to within r of the interface is,

$$\sigma_t = (F_t \sin\theta)/b = (R\mu_B b \sin\theta / 4\pi)(t_B - 2r)/[r(t_B - r)] \quad (4)$$

where θ is the angle between the interface and glide plane of B layer. If $t_B >> r_{\min}$ and $r_{\min} \approx 2b$, the maximum interfacial resolved stress is,

$$\sigma'_m \approx (R\mu_B \sin\theta)/8\pi = \sigma_m \sin\theta \quad (5)$$

$$\sigma_m = R\mu_B / 8\pi \quad (6)$$

Koehler calculated the resolved shearing stress σ'_m in table 1 for several material combinations satisfying the material conditions mentioned before.

It is shown that a maximum shearing stress of the order of $\mu_{low}/100$ will be obtained by the alternate layering of materials with high and low elastic constants. The low elastic constant material should have perfect dislocations rather than partial dislocations. In the case of a Ni/Cu combination, σ'_m having partial dislocation in Cu is $\mu_{Cu}/252$ but σ'_m having perfect dislocation in Cu is $\mu_{Cu}/102$. He used C_{44} as the modulus of rigidity (μ_A, μ_B) and noted that it is also valid if one of the materials is amorphous.

2. Hall-Petch relationship

The Hall-Petch relationship is a well-known empirical equation,

$$H = H_o + k_H d^{-n} \text{ or } \sigma = \sigma_o + kd^{-n}$$

where d is average spacing between the barriers to the dislocation motion and n is usually 1/2 in low temperature working condition. In case of microlaminate composite materials, d is the layer thickness of the laminates. Besides the effect of reduced layer thickness, it is also expected that the average grain size D in each layer is proportional to the layer thickness d ($D \approx d$) in thin films. Therefore, by reducing the layer thickness (d) smaller grain sizes can be produced and thus the strength and hardness will be increased.

III. Research

1. Lehoczky's work[14][15]

As Koehler proposed in eq. (5), the resolved shear stress was,

$\sigma'_m \approx (R\mu_B \sin\theta)/8\pi = \sigma_m \sin\theta$, where $\sigma_m = R\mu_B / 8\pi$

In the case of laminate having polycrystalline layers, the resolved tensile stress in B layers for yield is given by,

$$\sigma^B{}_a \approx \sigma_m + \sigma^B{}_\infty \quad (7)$$

$\sigma^B{}_\infty$: stress caused by frictional force in B as $d \to \infty$.

The applied stress required for yield should be greater than $\sigma^B{}_a$. In the elastic region, for a given strain ε, the applied stress σ_a is distributed between A and B layers,

$$\sigma_a = V_B Y_B \varepsilon + V_A Y_A \varepsilon \quad (8)$$

Y_A, Y_B : Young's moduli

V_A, V_B : Volume fraction of A and B layers.

The condition for yield is given by $Y_B\varepsilon \geq \sigma^B{}_a = \sigma_m + \sigma^B{}_\infty$, because the B layer is a soft material. The tensile stress is, therefore,

$$\sigma_a \geq (V_B + V_A Y_A / Y_B)\sigma^B{}_a = (V_B + V_A Y_A / Y_B)(\sigma_m + \sigma^B{}_\infty) \quad (9)$$

If $V_A = V_B$, that is equal layer thickness, the minimum yield stress is,

$$\sigma_a \geq (1/2)(1+Y_A/Y_B)\sigma^B{}_a = (1/2)(1+Y_A/Y_B)(\sigma_m + \sigma^B{}_\infty) \qquad (10)$$

With this theoretical background, Lehoczky produced data for Al/Cu and Al/Ag laminates.

- Deposition condition
  - E/B evaporation : two gun
  - S/S distance : 30cm
  - Substrate : NaCl single crystal, <100> direction
  - Substrate temperature : 25-40°C
  - Working pressure : $\approx 3\times10^{-4}$Pa
  - Deposition rate : 0.2-0.6nm/sec = 12-36nm/min

When comparing the mechanical properties of bulk Al and Cu to those of vacuum deposited coatings, the values of the latter were, Young's modulus of Al is the same as the bulk value but Cu is slightly lower than the annealed bulk value, yield strength of Al is a little higher than the annealed bulk value but Cu is much higher than the annealed bulk value, tensile strength of Al is higher than the cold worked bulk value and the same as Cu.

These results imply that the vacuum deposited films have already been strengthened by the reduced thickness (or grain size) and possibly by the imperfections caused by the low substrate temperature.

The theoretical yield strength was calculated to be 670Mpa, using the Young's moduli in vapor deposited thick films. Also it was 701Mpa using the bulk value. The latter will be probably more correct. Even though Lehoczky selected the highest measured values for a given layer thickness instead of the average value, it still shows some deviation from the theoretical value (612MPa, 701MPa respectively).

Lehoczky's data followed Koehler's theory well and also highlighted the concept of critical layer thickness. The correlation between stress and layer thickness below the critical thickness was t^{-1} in Fig. 2 but he also expressed the correlation as $t^{-1/2}$ in Fig. 3.

2. Springer's work[11][12][13]

As Koehler suggested in his paper, the critical layer thickness should be of the order of 100 atomic layers thick or less. Lehoczky's results were 232nm for Al (R_{Al}=0.286nm), 70nm for Cu (R_{Cu}=0.255nm) and over 240nm for Ag (Rag=0.288nm), i.e. about 200-800 atomic layers in order (R is atomic radius). In the following works such as Springer's and Bunshah's, the ranges of layer thickness were over 100nm. So the variation of the strength with layer thickness is expected to follow the Hall-Petch relationship.

Springer used the PGP (pulsed gas process) to make laminates in Al/Al oxide[11], Al/Al nitride[12], This idea is to inject gas during the deposition of metallic films with repeated time intervals. By this method laminates of metal/metal oxide or nitride (possibly carbide) can be produced. The strong point of this process is the simplicity of the deposition equipment, one evaporator instead of two evaporators for two composition.

Fig. 4 and Fig. 5 are the result for Al/Al oxide laminates, showing the Hall-Petch type relationship between the measured yield strength (σ_y) and laminate spacing (d). The data in Fig. 4 shows a straight line on a log-log plot of σ_y versus d. The slope of the line is -1/2. Fig. 5 shows the replot for σ_y versus $d^{-1/2}$. The interesting result is that the yield strength data seems to be constant for layer thickness of 100-200nm which includes the critical layer thickness for Al suggested by Lehoczky(232nm). Springer didn't note this and thus further interpretation is impossible. However below this thickness, it still shows a straight line. He reported grain refinement during the growth of layers resulting from the suppression of columnar growth. Ahmed[18] also reported the same result by X-ray diffraction and TEM analysis. The crystallinity of Al decreased as the oxygen flow increased. The grain size changed from 1μm in the absence of oxygen to 0.25μm at the flow of oxygen.

Springer also tried to make Al/Al nitride laminates. Fig. 6 shows the Hall-Petch relationship. The difference between the oxide and nitride laminates is the flow stress σ_0 and a slight change in k value. He explained this as being a result of grain refinement, but submitted no data. The difference started from specimen preparation : the nitride was deposited by sputtering but the oxide by evaporation. The degree of damage in the growth layer would be quite different from each other, and also the microstructure and the internal stress.

Fig. 7 shows another Hall-Petch type relationship for Ta/Ta carbide laminates by Springer. During the evaporation of Ta, the carrier gas was pulsed as a source of carbon. The striking feature in these laminates is that there is no evidence of carbide in the layers. He also didn't identify whether the carbon was interstitial or substitutional, but he did find a difference in grain size and a separate class of grains between the pure Ta layers and pulsed Ta carbide layers. Fracture strength instead of yield strength was measured because the laminate fractured before yield.

Springer suggested an alternative method to produce laminates. This was changing the deposition parameters so as to alter the growth structure, as in Thornton's growth model.

3. Bunshah's work

The systems he studied are summarized below :

Metal/metal systems

1) Ni/Cu : composite solid solubility, same crystal structure
2) Fe/Cu : negligible solid solubility different crystal structure
3) Ti/Ni : brittle intermetallic compound

Metal/ceramic systems : TiC/Ni

Ceramic/ceramic systems : TiC/TiB

- Deposition condition
  - Two E/B gun evaporator source
  - Temperature : $\approx 0.4\text{-}0.45T_m$
  - Working pressure : $1\times10^{-4}\text{-}1\times10^{-5}$Torr
  - Laminate thickness : ≈0.2-30μm
  - Total thickness : ≈0.2-0.8mm

Fig. 8 shows a schematic diagram of the deposition apparatus. The main features are the water cooled separating wall and the control of laminate thickness by the rotation speed of the substrate disk and evaporation rate from the source. The average laminate thickness (A+B layers) can be easily obtained by dividing the total thickness into the number of rotations.

In Fig. 9(a) and (b), the values of microhardness and tensile strength of Fe/Cu laminate are plotted against $\delta^{-1/2}$ where δ is the laminate thickness. The microhardness and tensile strength begin to increase abruptly for layers less than 1μm thick. With 0.45-0.50μm thick layers, the maximum value of tensile strength is presented. A further decrease in the layer thickness also reduces the tensile strength. The possible cause of this tensile strength reduction is considered to be the mechanical unstability resulting from the inner stress at the Fe/Cu interface. Comparing with the Ni/Cu system, the Fe/Cu system has a different crystal structure, larger difference in lattice parameter and a weak bond strength between Fe and Cu atoms due to the negligible mutual solid solubility.

In Fig. 10 and Fig. 11 the variation of yield strength and microhardness of Ni/Cu laminates are plotted against $\delta^{-1/2}$. Both features show good Hall-Petch type correlation. The X-ray intensity profile of Cu/Ni along the thickness of the laminate deposited at 625°C shows that there was extensive interdiffusion of copper and nickel : the yield strength reduction at 400 °C in Fig. 10 can thus be explained. This Ni/Cu system did not have a maximum in the yield strength, like the Fe/Cu system.

IV. Conclusion

To optimize the strengthening effect in microlaminate composite materials, One must conduct materials selection, design of laminate structure and process control. For the materials selection, the elastic constants of A and B materials should be different as much as possible in order to confine dislocations in low elastic constant material and the interfacial strain should be small not to destroy the laminate structure at the interface. For design of laminate structure, there is an critical thickness which is an internal property of materials. Koehler's suggestion of thickness less than 100 atomic layers encourages this approach. For process control, the promising process to produce thin layered microlaminate composite materials will be physical vapor deposition (evaporation, sputtering and ion plating). Each process has its own strong points and also limitation. It is necessary to overcome the interfacial strain between the layers to achieve the strengthening effect by adequate process control.

V. References

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Table 1. Calculation of resolved shearing stress of material combinations.

Material combination(A/B)	R	σ'_m	Remarks
Ni/Cu	0.2466	$\mu_{Cu}/102$	Both FCC, complete dislocation
Ni/Cu	0.2464	$\mu_{Cu}/252$	Both FCC, partial dislocation in Cu
Rh/Pd	0.547	$\mu_{Pd}/56$	Both FCC, complete dislocation
MgO/LiF	0.404	$\mu_{LiF}/87$	Alkali halide, complete dislocation
W/Ta	0.2946	$\mu_{Ta}/121$	Both BCC, complete dislocation

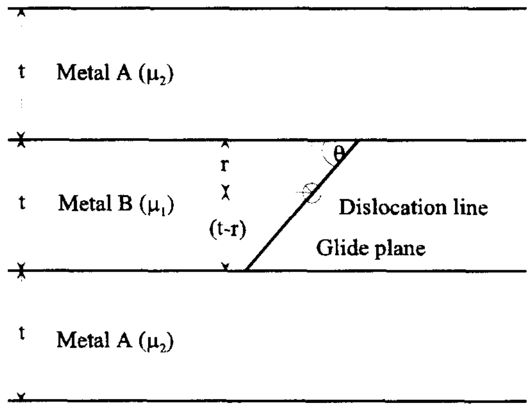

Fig. 1. Geometry of dislocation line and glide plane in a metal layer.

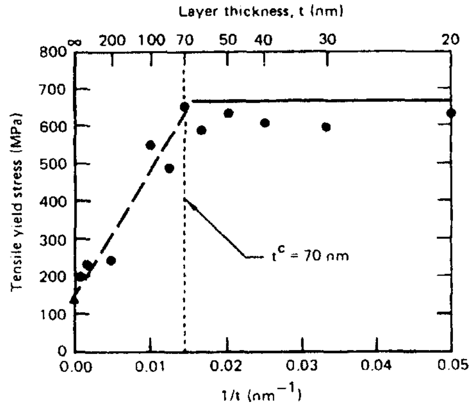

Fig. 2. Inverse layer - thickness dependence of the tensile yield stress for Al-Cu laminates. The Al and Cu layer thickness were equal in each laminate. The solid triangle is the value given by the rule of mixtures for thick films of the metals. The solid line is given by Eq. (9). The critical layer thickness is about 70nm.

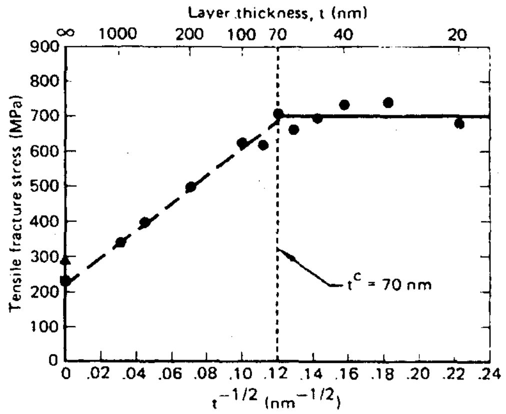

Fig. 3. Inverse layer-thickness dependence of the tensile fracture stress for Al-Cu laminates. The Al and Cu layer thickness were equal in each laminate. The solid triangle is the value given by the rule of mixtures for thick films of metals. The solid square is the value given by the rule of mixtures for cold rolled bulk metals. The critical layer thickness is about 70nm.

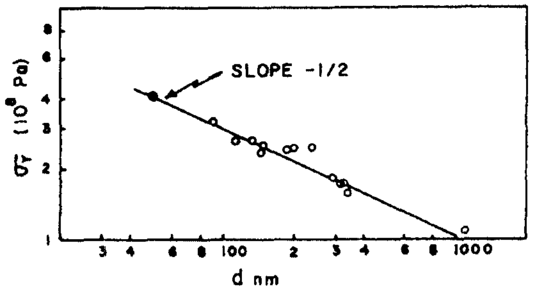

Fig. 4. A log-log plot of the yield stress vs. The layer spacing gives essentially a straight line. The line has a slope approximately equal to -1/2.

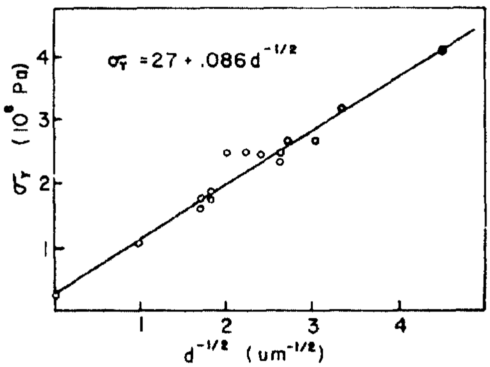

Fig. 5. The yield stress and layer spacing are plotted on a linear ordinate and reduced abscissa. It is increasing to note that the experimental line intersects the yield stress for a pure specimen. The equation gives the yield stress in megapascals for 5-10 at.% oxygen in the oxide layer.

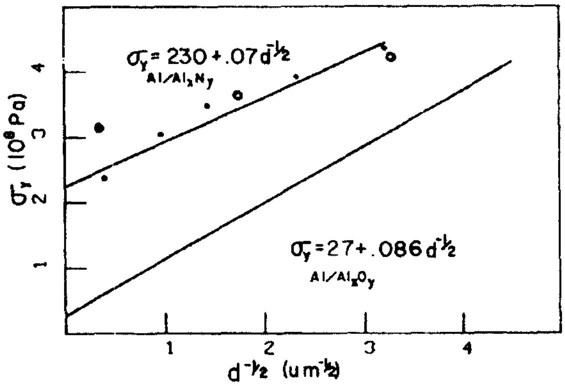

Fig. 6. The yield stress as a function of layer spacing is plotted. The yield strength found for the Al/Al$_x$O$_y$ is plotted for a reference. The essential difference in the curves is value of the drag stress σo. The open circles are the values of yield stress obtained from the rotating cylinder. The yield strengths are not degraded as with the oxide coatings.

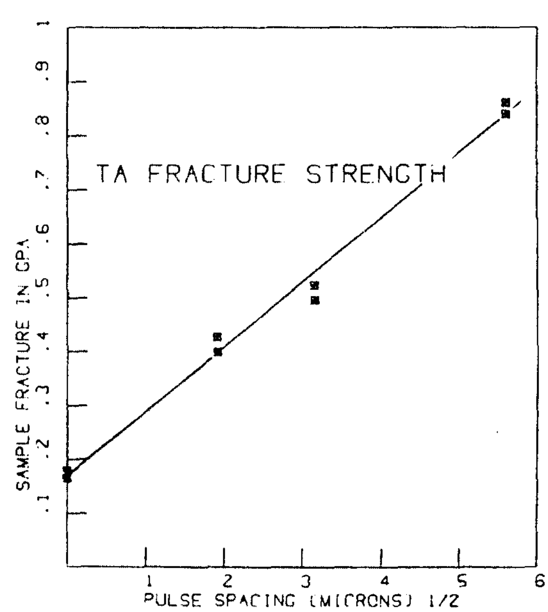

Fig. 7. The fracture strength of the tantalum specimens are plotted against the pulse spacing to the -1/2 power. It is fortuitous that the data fall essentially on a straight line giving a Hall-Petch type dependence. The most significant result is the strength enhancement of about five times.

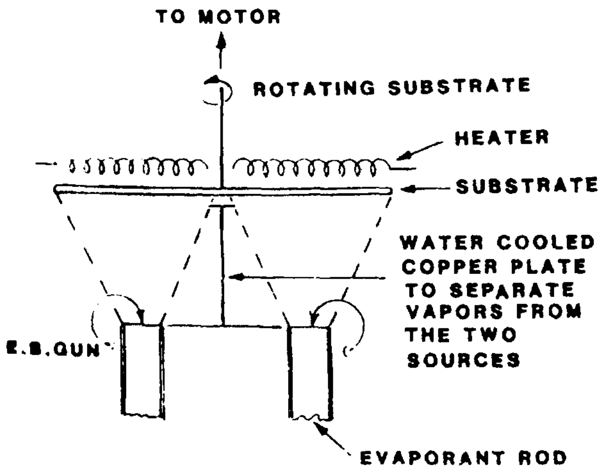

Fig. 8. Schematic diagram of the vacuum evaporation apparatus with two sources for depositing laminate composites on a rotating substrate.

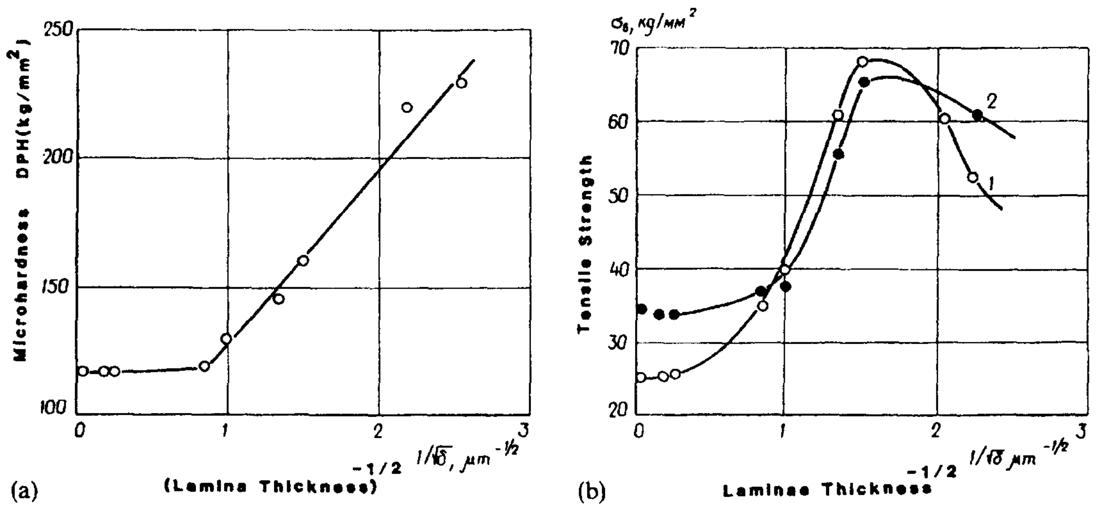

Fig. 9. (a) Plot of the microhardness against (the thickness of the laminae) $^{-1/2}$ in the Fe-Cu system ; (b) plot of the tensile strength against (the thickness of the laminae) $^{-1/2}$ in the Fe-Cu system.

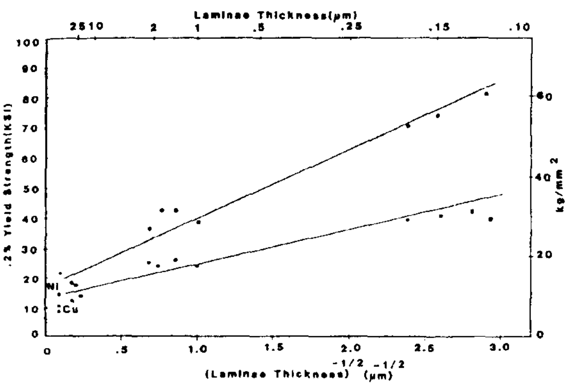

Fig. 10. Plots of the 0.2% yield strength against (the thickness of the laminae) $^{-1/2}$ in the Cu-Ni system ; O,●, at 25°C ; □, ■, at 400°C.

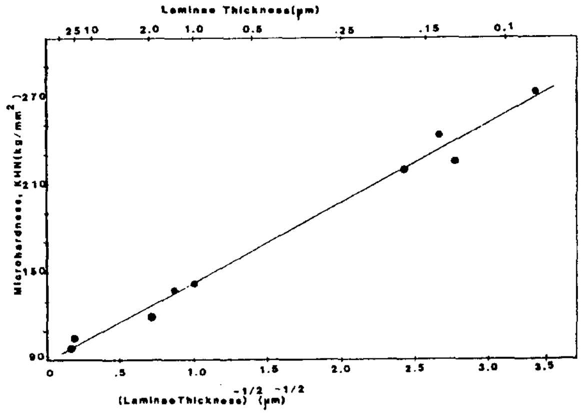

Fig. 11. Plot of the microhardness against (the thickness of the laminae) $^{-1/2}$ in the Cu-Ni system.