PM**I**
MA
1996

"The Physics and Modelling of Intelligent Materials and their Applications"

(PMIMA).

Proceeding of the Russian-Japanese joint seminar

N.S.Perov, A.A.Radkovskaya (editors)

Faculty of Physics
Moscow State University
19-22 September 1996.

MOSCOW
1996

Preface.

The Russian-Japanese joint seminar "The Physics and Modelling of Intelligent Materials and their Applications" (PMIMA) was held from 19 through 21 September 1996 at the Faculty of Physics of Moscow State University in Moscow, Russia.

The seminar aimed to discuss various subjects on fundamental and applied problems on intelligent materials and connected topics.

The seminar gathered 61 participants (13 of them were from Japan). Russian participants were from Moscow University (faculties of physics and chemistry and institute of mechanics), Chelyabinsk and Vladikaukaz Universities, Baikov Institute of Metallurgy, Moscow institute for Radioengineering Electronics and Automation, Troitsk Institute for Innovation and Fusion research and other divisions of Russian Academy of Science. 43 papers were presented that were contributed by 122 authors.

The scientific program included 6 oral sessions and a poster session. Besides there were carried out an excursion over the scientific laboratories of the faculty of physics of the Moscow University.

The seminar has demonstrated the difference between Russia and Japan in that which can be called as "fundamental" and "applied" approaches. The seminar allowed to get the best from both approaches in our countries. The following list shows possible joint research projects that can be initiated soon:

a) ferromagnetic shape memory alloy;

b) non—destructive testing;

c) biomedical applications;

d) high-T_c superconductors.

I would like to thank all of the people who contributed to the success of the seminar. Especially I appreciate the essential contribution of professors Tani J. and Takagi T. from Tohoku University (Japan).

N.S.Perov
Program Committee Chairman

THE TERMAL TREATMENT EFFECT ON PHYSICAL PROPERTIES OF AMORPHOUS METALLIC ALLOYS

S.G.Zaichenko[a], V.M.Kachalov[a], A.M.Glezer[a], E.A.Gan'shina[b], N.S.Perov[b], E.V.Kim[b], S.N.Sazonova[b]

[a] Department of Metal Physics, I.P. Bardin Central Research Institute of Ferrous Metallurgy, 2 Baumanskaya, Moscow 107005, Russia
[b] MSU, Department of Physics, Leninskiye Gory, Moscow, Russia

Abstract

Ductile-brittle transition in amorphous metallic alloys (AMAs) based on Fe-Ni, Fe-Co and Fe-Ni-Co after definite temperature-time actions has been investigated. Embrittlement begins from the ribbon surface and embrittled layers thickness is a function of thermotreatment parameters. The criterion for the beginning of ductile-brittle transition has been established. Structural difference between embrittled layers amorphous state and plastic amorphous core has been established by magnetic, magnetooptical, spectroellipsometric neasurements and Auger spectroscopy. Experimental data let us to propose new amorphous phase formation in the embrittled layers.

Keywords: Amorphous metallic alloys, ductile-brittle transition, mechanical behaviour, relaxation spectrum, plasticity.

Introduction

It is well known that amorphous metallic alliys (AMAs) exist in a metastable equilibrium state. That is under the influence of such destabilizing factors as temperature, time, irradiation with particles of different nature they lose their initial plasticity and change to the embrittled state [1,2]. In the present work temperature T and time τ will be primary considered as the destabilizing factors.

AMA ductile-brittle transition is a process developing in time dependent on intensity and time of destabilizing actions. It was established in [3,4,5] that AMA embrittlement starts from the ribbon surface, the thickness of embrittled layers is a function of temperature and duration of AMA annealing; removement of embrittled layers from the surface by any method (mechanical treatment, electropolish, etching, etc.) leads to the full recovery of initial plasticity.

Ductile-brittle transition is described as free volume exit on the AMA surface in most papers [6]. But further investigations of embrittled layers by various structural analysis methods [7] showed that these layers are in an amorphous state different from the initial one (and, consequently, from that of the amorphous core). This fact can not be explained exclusively by free volume exit.

So, in this paper we present our investigations of AMA embrittled layers structure and microscopic proceses accompanied ductile-brittle transition to develop physical model of the last.

Experimental details.

Ribbon specimens of AMAs of three different compositions based on $Fe_{81.8}Ni_{10}Si_{5.2}B_{3.0}$ (a), $Fe_{5.7}Co_{83.5}Si_{8.6}B_{2.2}$ (b), $Fe_{5.7}Ni_{12.2}Co_{72}Si_{6.5}B_{3.6}$ (c) and doped with metalloids Si and B were obtained by spinning method. The AMAs samples, 20 mm wide and 20 to 25 μm thick, were subjected to isochronic annealings (τ=10 min) in the temperature range from 473 °K to 750 °K with 20 °K steps. To obtain each point on the ε_f–T_a plot, where ε_f is the relative deformation at failure and T_a is the annealing temperature, 30 specimens were mechanically tested, what assures the 95% confidence level. The relative deformation at failure was calculated as ε_f=d/(D–d), where d is the ribbon thickness, D is the distance between micrometer plates at the instant of failure of the half–loop of the bent ribbon specimen. For specimens in the initial state ε_f was believed to be equal to 1 (true value ε

Fig. 1. Dependence of the relative deformation at failure (ε_f) on the isochronic annealing temperature for AMA (b).

f(true) $=1.234 \times \varepsilon_f$ [8]). Temperature T_a=573 °K on Fig.1 corresponds to the beginning of ductile-brittle transition and from this point ε_f value sharply drops with T_a increase. From T_a=623 °K ε_f decreases slightly when T_a raises and forms a shoulder, Fig.1.

The temperature range T_a=573–623 °K corresponds to a "half–embrittled" AMA state where some part of the specimens group (30 pieces) is failed while other remain plastic. This phenomenon is explained, first of all, by variations in the ribbon thickness amounting up to 10% of the average value.

Small decrease of ε_f from T_a=623 °K is explained by the increase of the thickness of surface ribbon layers losing their plasticity. This thickness is a function of the alloy composition, annealing temperature and time [9]. The removal of those layers by any method (etching, electropolishing, machining) results in the complete restoring of the initial plasticity that is confirmed by residual bend angle appearance under tests of free bending by 180 degree .

The evolution of activation energy of the spectrum at the increasing temperature of isochronic annealings was studied on specimens of alloys above mentioned immediately after mechanical tests. The measurements were performed by the differential scanning calorimetry (DSC) using Du Pont thermoanalyzer.

A rapid decrease of the low–temperature part (up to T_a ≈638–648 °K) of relaxation spectrum while the high–temperature one (from 638–648 to 673–703 °K) remains essentially unchanged is a main feature of the evolution of the spectrum of activation energy in the region of ductile-brittle transition, Fig.2.

In low–temperature part of relaxation spectrum some areas have appeared where heat emission reverseds a sign.

Comparing the results of AMA mechanical tests (Fig.1) with the heat structure relaxation heat of low–temperature spectrum range

$$Q_l = \int_T h(T_a, T, \tau)dT \qquad\qquad (1)$$

as a function of T_a we have obtained a criterion of the beginning of AMA ductile-brittle transition. This criterion has a form

$$Q_l = \int_{T_l}^{T_h} h(T_a, T, \tau)dT = 0 \qquad\qquad (2)$$

where the lower integration limit (T_l) corresponds to the temperature of the beginning of structure relaxation; and the upper integration limit (T_h) corresponds to the temperature of upper limit of the low-temperature part of relaxation spectrum. Similar results were obtained for AMAs of different compositions. Thus, zero structure relaxation heat of low-temperature part of relaxation spectrum is the criterion of the beginning of AMA ductile-brittle transition.
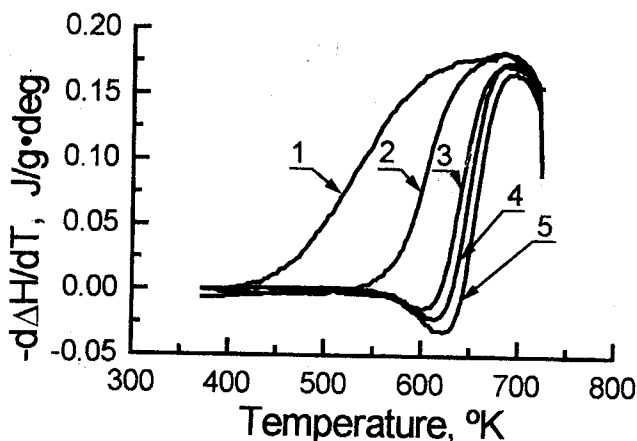

Fig. 2. Variation of the spectrum of activation energy for AMA (c) at isothermal annealing T_a=573 °K for specimen in initial state, (1), annealed for τ=1 min, (2), τ=40 min, (3),τ =90 min, (4), and τ=180 min, (5), specimens (4) and (5) are embrittled.

Comparasion of structure relaxation heat of low-temperature part of relaxation spectrum for embrittled AMA specimens and specimens after removing of embrittled layers was made for verification of criterion (2), Fig.2. In the cases 4 and 5 (Fig.2) structure relaxation heat of low-temperature part of relaxation spectrum reverses the sign, namely, $Q_l<0$ for embrittled samples and $Q_l≥0$ for samples after removing embrittled layers. Thus, all these experiments confirm the validity of the criterion (2).

Measurements of relative density $\Delta\rho(T_a,T,\tau)$ of AMA (b) studied in the initial state and after annealing at T_a=673 °K during τ=10 min and τ=360 min were carry out dilatometrically. In the last case all sumple material was embrittled because its plasticity did not restore at any thinning. The measurements were performed in dilatometric contrivance to Du Pont thermoanalyzer.

Heating rate was minimal, namely ~5 °K in min, accuracy was ±10⁻³ µm. We have determined density changes with high level of precision from samples elongations during heating on the basis of the fact that specimens length was > 10³ as much as their thickness and 15 as much as their width. Differences between absolute elongations

$\Delta l_{(1)}=\Delta l_1-\Delta l_2$; $\Delta l_{(2)}=\Delta l_1-\Delta l_3$, were compared, where Δl_1 is the elongation of a sample in the initial state, Δl_2 is the elongation of annealed sample ($\tau=10$ min), Δl_3 is the elongation of annealed sample ($\tau=360$ min). It should be noted that Δl_1 was a linear function of T. The extremum values of $\Delta l_{(1)}$ and $\Delta l_{(2)}$ occured in the temperature regions $\Delta T=343-393$ °K and $\Delta T=423-523$ °K respectively, with extremum at T=343 °K and T=483-493 °K, where Δl_1 and Δl_2 were opposite in sign. From T=650 °K ductile flow of samples owing their weight was observed. Changes in relative density $\Delta\rho$ were estimated on the assumption of the exit of free volume excess part through ribbon surface:

$$\Delta\rho\approx2\times\Delta l/l_0 \tag{3}$$

From Eq.(3) values $\Delta\rho_{max}=0.08-0.12\%$ were calculated coinsiding with the results obtained in [1]. Dilatometric studies have shown that just as the first density changes for samples in the initial state take plase at temperatures lover the temperature of ductile-brittle transition (T=573 °K) so maximal $\Delta\rho$ takes place at the temperature lower than this transition onset. Our measurements show that for AMAs studied $\Delta\rho$ changes are not necessary related with AMAs ductile-brittle transition and contrary to data of [1] have no jumping character but change step by step in wide temperature region.

Spectral-ellipsometric study of AMA (a) samples in the initial state and after their embrittling annealing were achived using ellipsometer AEF-3M-I. Working light wavelength of Helium-neon lazer was $\lambda=632.8$ nm. Angle-dependences of ellipsometric parameters including fase shift Δ between p– and s– components of polarization vector were measured. On their base the main angle φ_0 (that is the angle corresponding to $\cos\Delta=0$) was calculated. It was established that a jumping change of φ_0 value corresponds to the moment of ductile-brittle transition and the following T_a increase leads to φ_0 decrease.

Some differences between the atomic-spectral structures of samples studied in the initial and embrittled states were established using spectroellipsometric study from spectral dependence of optical conduction in the range 0.5–4 eV. Optical conduction spectrum is mainly determined by frequency of the γ–electrons collision with medium microinhomogeneities having dimentions of some hundered Å. From these data we concluded that clusters forming in embrittled layers.

The changes of magnetic characteristics of AMAs (a-c) after ductile-brittle transition were investigated on the samples after isochronic annealings ($\tau=10$ min, $T_a=623$, 648 and 673 °K). The alloy (b), magnitostriction of which is equal to zero, was investigated in considerable detail, [10]. For the control these changes were compared with magnetic characteristics of the alloys in the initial state.

The following characteristics were measured: saturation magnetization, hysteresis loops, angle delay of magnetic moment in rotating external magnetic field of various intensity, and magnetooptical spectra of the reflection (Kerr effect). Magnetostatic results were obtained on vibroanizometer and magnetooptical ones – on spectralmagnetooptical unit.
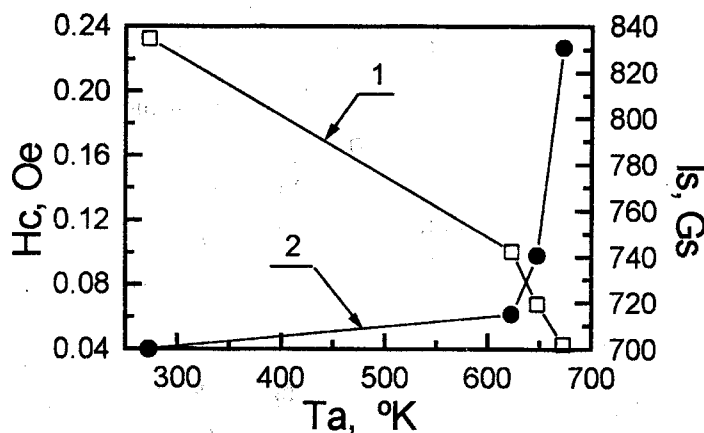
Fig. 3. Dependence of the coercive force, H_c, and the saturation magnetization, I_s, on annealing temperature T_a for AMA (c): 1- H_c, 2 - I_s.

The dependences of saturation magnetization I_s and coercive force H_c on the annealing temperature T_a are given in Fig.3. Fig.3 shows a significant decrease of the coercive force and increase of saturation magnetization with T_a. This proves that the samples becomes more homogeneous. Samples homogenization is caused by significant influence of internal demagnetization field on internal demagnetization field which in its tern affects the magnetization inspite of small thickness of band samples (20–25 μm). The value of demagnetization factor being of ~28×10^{-4}π corresponding to the ratio of thickness of the samples to their diameter, of about ~5×10^{-4}. This leads to the appearance of internal fields of $4\pi \times I_s \approx 6$–10 Oe in saturation, which significantly exceeds H_c of the band samples. It is possible to conclude already from these data that embrittling annealing leads to appearance of new amorphous phase with large magnetization magnitude.

The curves of angle delay depending on T_a in the external magnetic fields of various intensity are given in Fig.4. All curves (H_{ext}=1, 2, 4, 8, 16, 32 Oe) were obtained for each sample (annealed and in the initial state) we present only six curves on Fig.4 (two for each annealed sample) which are representative of behavior observed.

The analysis of that curves shows the following: in the external field $H_{ext}<1$Oe all the samples demonstrate one-direction anisotropy the magnitude of which depends on T_a. T_a growth leads to anisotropy decrease. The presence of one-direction anisotropy evidents the formation in the annealed samples of the inclusions (clusters of new amorphous phase) with anisotropy fields exceeding in two times H_{ext}. One-direction anisotropy was observed on the samples in the initial state at the fields $H_{ext} \leq 8$ Oe. Besides, in the samples after annealing at T_a=623 and 628 °K the uniaxial anisotropy appears which changes together with one-direction one to quadrupole. This anisotropy practically disappears at T_a=673 °K. The appearance of uniaxial anisotropy, in our opinion, can be explained by the formation in the embrittled layers of the inclusions of phase with shape anisotropy. The uniaxial anisotropy decrease at $T_a \geq 673$ °K evidents the termination of the formation of the embrittle layers with critical size leading to full embrittlement during mechanical tests.
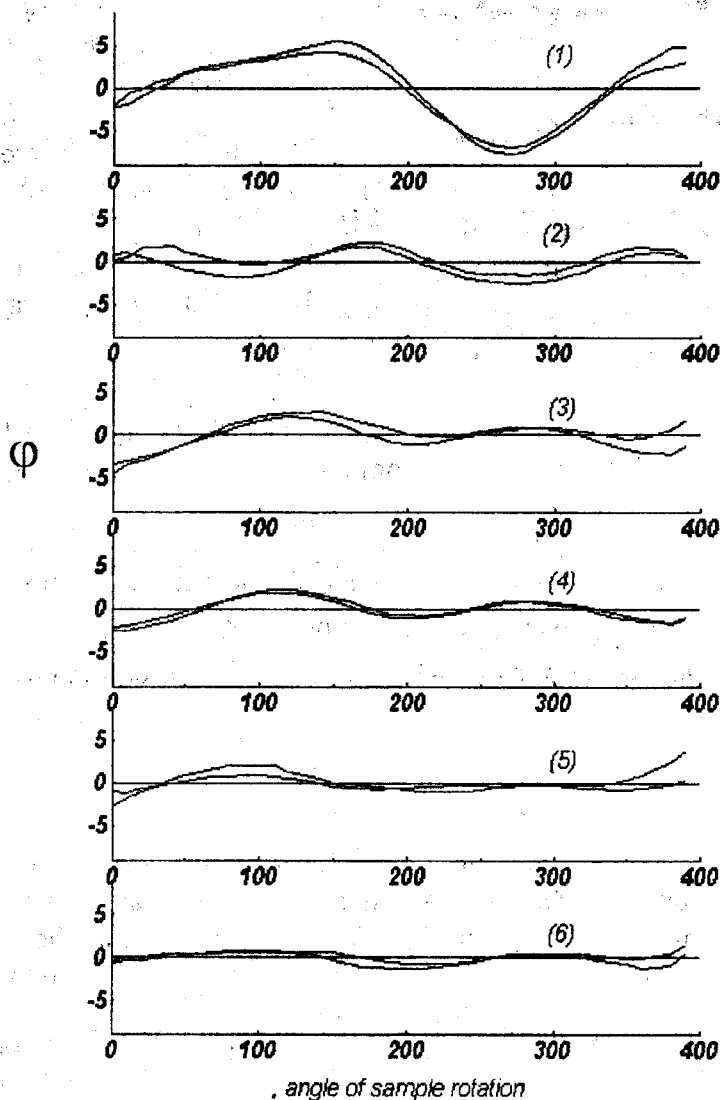
Fig.4. Curves of angle delay depending on T_a in external magnetic fields of various intensity:

T_a=623°K, H_{ext}=1 Oe, (1);

T_a=623°K, H_{ext}=16 Oe, (2)

T_a=648°K, H_{ext}=1 Oe, (3)

T_a=648°K, H_{ext}=16 Oe, (4)

T_a=673°K, H_{ext}=1 Oe, (5)

T_a=673°K, H_{ext}=16 Oe, (6)

φ is the magnetic moment deflection

The dependence of the hysteresis of angle delay on the field proves also the appearance of a fraction with high anisotropy at T_a=623 °K with I_s~17 Oe. In this case I_s at T_a=648 °K is in the area of higher fields, and it practically disappears at T_a=673 °K. We believe that the appearance of anisotropy is caused by the formation of new phase in embrittled layers. Increase the new phase with initial small sizes grows at T_a (and anisotropy grows too), and from $T_a \geq 623$ °K the tendency to the structural homogenity is observed as new phase reach maximal sizes, and/or it means that embrittled layers containing new phase are significant part of all the volume of the samples.

The assumption about the formation of new phase in embrittled layers is confirmed by the dependence of magnetooptical spectra (Kerr effect) on T_a, Fig.5.
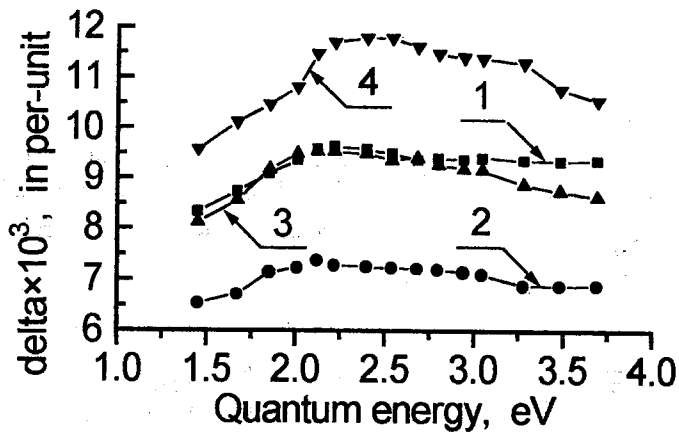
Fig. 5. Dependence of magneto-optical spectra on annealing temperature: in initial state (1), T_a=623 °K (2), T_a=648 °K (3), T_a=673 °K (4).

The Kerr effect slightly decreases at T_a=623°K and then during T_a increase up to 60% of minimal value. This increase is partially connected with magnetization growth, but the most significant contribution is connected with the formation of new phase, where the Fe-atoms are in octahedral surrounding, which is visually demonstrated in Fig.5. The effect decrease of T_a=623 °K at practically constant I_s is an additional proof that structural changes (new phase formation) takes place in surface zones, or, in other words, in the embrittled areas of the material.

During the removal of embrittle layers by chemical etching the saturation magnetization of the samples I_s grows with the thinning of the samples independent on T_a (correspondingly, embrittled layers thickness grows with T_a growth, so it is necessary to remove a large amount of material) and it gradually approaches to I_s of the samples in the initial state.

Discussion.

Thus, from the above data we can reveal the following features of ductile-brittle transition in AMAs of metal-metalloid type. AMAs ductile-brittle transition occurs in time and finishes by joining of growing embrittled layers that is when a whole ribbon material becomes embrittled. This process begins from the ribbon surface, the thickness of the layers loosing their plasticity is a function of intensity and duration of destablizing temperature-time actions. Embrittled layers occure in an amorphous state different from the initial state. At the same time physical characteristic of the amorphous core remain identical to that of the initial state.

Ductile-brittle AMAs transition is characterized by crash drop of failure deformation in 15-20 times. This mechanical degradition is mainly caused by structural changes in embrittled layers, namely, by new amorphous phase formation. According to Auger spectroscopy and spectroellipsometric data [11,12] these new regions have dimentions of an order of same tens nm and a needle or a disk form (from magnetic study data) [10].

New amorphous phase has a chemical composition different from that of the initial state. All data of Auger and magnetic study (magnetostatic and magnetooptical measurement) confirm this. Moreover, its magnetic characteristics and X-ray microprobe data differ from that of the initial material. It is in good agreement with the data of [1] in which Curie temperature, T_C, other than T_C of initial samples was observed.

We have suggested that crash embrittlement of AMAs in the moment of their ductile–brittle transition is caused not only by the exit of the excess part of free volume on the surface (according to our dilatometric study data) but by the fact that fracture stress of embrittled layers containing new phase is smaller than their yield stress. New phase inclusions concentrate stresses, and stress concentration coefficient may vary from 3 up to ∞ according both the moment elasticity theory [13,14] and micropolar medium theory [15] depending on the inclusions dimentions, concentration, amorphous layers thickness and relation between Young modules and Poisson's ratio of the inclusions and amorphous matrix.

The detail study of these aspects will be the item of our future work.

Conclusions.

Our study of AMAs ductile–brittle transition let us to conclude:
(i) ductile–brittle transition is a developing in time process of embrittled layers growth from the AMA ribbon surface;
(ii) embrittled layers contain new amorphous phase differing from the initial state by the chemical composition and physical properties;
(iii) the criterion for the beginning of ductile–brittle transition is the equality to zero of the low–temperature part of the relaxation spectrum.

References

[1] R.Gerling et.al, *Acta Metall.*, *36* (1988) 575.

[2] D.G. Ast, D. Krenitsky, *Mater. Sci. Eng.*, *43* (1980) 241.

[3] S.G. Zaichenko et.al., *Izv. AN.Metally, No 4* (1992) 165, (in Russian).

[4] S.G. Zaichenko, V.M. Kachalov, *Function. Mater.*, *2* (1995) 232.

[5] S.G.Zaichenko, V.M.Kachalov, to be publ. in *Phis. Chim. Mater. Treatment, No 4* (1996), (in Russian).

[6] A.M. Glezer et.al., *FMM, 58* (1984) 991, (in Russian).

[7] S.G. Zaichenko et.al., *Proc. 12th Ukraine school-seminar on Spectroscopy of Molecules and Crystals 3-8 July, Nejin, KSU,* (1995) 69.

[8] S.G. Zaichenko et.al., *Labor. Indastry, 55* (1989) 579.

[9] S.G. Zaichenko, V.M. Kachalov, *Metally, No 3* (1994) 113.

[10] E.A. Gan'shina et.al., to be publ.

[11] J.L. Walter et.al., *Mater. Sci. Eng.,* *24* (1976) 239.

[12] F. Okuyama et.al., *Appl. Phys., 60* (1986) 2618.

[13] Y. Weitsman, *Transact. Amer. Soc. Mechan. Eng., E32* (1965) 424.

[14] Y. Weitsman, G.C. Sih, *Transact. Amer. Soc. Mechan. Eng., E32* (1965) 429.

[15] P.N. Kaloni, T. Ariman, *ZAMP, 18* (1967) 136.