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DIVISION OF APPLIED SCIENCES

DAVID TURNBULL
GORDON McKAY PROFESSOR OF APPLIED PHYSICS

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(NASA-CR-162075) CRYSTAL NUCLEATION IN GLASS-FORMING ALLOY AND PURE METAL MELTS UNDER CONTAINERLESS AND VIBRATIONLESS CONDITIONS Annual Report (Harvard Univ.) 15 p HC A02/MF A01 CSCL 11F G3/26

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National Aeronautics Space Administration
G.C. Marshall Space Flight Center
Marshall Space Flight Center
Huntsville, AL 35812

ATTN: AP29H

Enclosed you will find a copy of the Annual Report for NASA Contract NAS8-32691.

A copy of this letter and report have been forwarded to the following:

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Sincerely,

David Turnbull

David Turnbull
Principal Investigator

DT:jav
enc.
cc: Dr. McKinney/HU
M. Lerman/HU
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NATIONAL AERONAUTICS SPACE ADMINISTRATION

ANNUAL REPORT

JULY 1982

Under Contract No. NAS8-32691

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CRYSTAL NUCLEATION IN GLASS-FORMING ALLOY AND PURE METAL MELTS UNDER CONTAINERLESS AND VIBRATIONLESS CONDITIONS

Prepared For

George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama 35812

Prepared By

Frans Spaepen/David Turnbull

Division of Applied Sciences

Harvard University - Cambridge, Massachusetts

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Our research during the past year has been on the following topics:

1. Bulk Formation of Metallic Glasses.
2. Theory of Transient Nucleation
3. Dilatometric Measurements on Pure Metal Dispersions.

These topics are discussed in sequence.

1. Bulk Formation of Metallic Glasses

Our earlier work, described in previous reports, has indicated that the homogeneous crystal nucleation frequency is low in alloys with high glass transition temperatures, T_g, relative to their liquidus temperatures, T_ℓ. Our theoretical calculations, based on classical nucleation theory combined with simple solution models for the crystalline and liquid phases, indicated that homogeneous nucleation would be negligible in alloys with $T_{rg} = T_g/T_e > 0.6$. Our drop tube experiments on $Pd_{82}Si_{18}$ alloy droplets (T_{rg}=0.60) confirmed that the homogeneous nucleation race is quite low ($< 10^5$ nuclei/cm^3.sec) and glass formation could occur at cooling rates of less than 800 K/sec. When crystallization was observed, it was heterogeneously nucleated at the droplet surface.

We have therefore, investigated the undercooling behavior of large spheroids of $Pd_{40}Ni_{40}P_{20}$ because of its exceptionally high T_{rg} (0.67). By surface etching, supporting the specimens on a fused silica substrate, and successive heating and cooling in a 10^{-6} torr vacuum, crystallization could be eliminated, presumably due to the removal of surface heterogeneities By this method samples up to 3.2g, with a 0.53 mm minor diameter, have been made entirely glassy, except for some superficial crystals comprising less than 0.5% of the volume. These experiments show that a cooling rate of ~1 K/sec is adequate to avoid copious homogeneous

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nucleation in this alloy, and that by eliminating or reducing the effectiveness of heterogeneous nucleation sites, it should be possible to form bulk samples of this metallic glass with virtually unlimited dimensions. A paper by Drehman, Greer and Turnbull describing these results is attached as an appendix and will be published in Applied Physics Letters.

We have also investigated the undercooling behavior of a number of Fe-based glass forming alloys ($Fe_{40}Ni_{40}B_{20}$, $Fe_{40}Ni_{40}P_{14}B_6$, -- $Fe_{79.3}B_{16.4}Si_{4.0}C_{0.3}$). Droplets down to 0.25 mm diameter were solidified in our 3 m drop tube, and were found to be fully crystalline.

2. Theory of Transient Nucleation

The thesis work of Thompson, described in earlier reports, has given experimental and theoretical indications of the importance of transient crystal nucleation, i.e. the nucleation process prior to establishment of steady state homogeneous nucleation. For example, it was necessary to introduce a non-zero transient time to account for the devitrification kinetics of $(Au_{1-x}Cu_x)_{77}Ge_{14}Si_9$ alloy glasses. The theoretically calculated values for the maximum steady-state homogeneous nucleation rate in glass forming alloys with $T_{rg} \simeq 0.5$ (such as Fe_4B) are about 10^{15} nuclei/cm^{3}sec; that these alloys can still be made glassy at cooling rates of only 10^6 K/sec can therefore only be explained by an appreciable transient period prior to steady state nucleation.

We have therefore initiated a theoretical study of the kinetics of transient nucleation. An exact solution of the coupled differential equations describing the dynamics of the embryo population in the non-steady

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state regime has been obtained for a one-component system at constant temperature. An alternative method, which is mathematically simple and more easily applicable to non-isothermal conditions or multi-component systems, has been shown to give time-dependent embryo populations that are in good agreement with the exact solution. A paper by Kelton, Greer and Thompson presenting these results and comparing them to earlier analytic work is in preparation.

3. Dilatometric measurements on Pure Metal Dispersions

We have recently begun a series of measurements, using the high-precision dilatometer built earlier by Thompson, on dispersions of Hg and Ga with different surface coatings in order to determine the possible effect of large negative pressures on the thermal expansion and nucleation temperature. So far we have succeeded in obtaining large undercoolings with one Ga dispersion.

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PUBLICATIONS:

1. A.J. Drehman and D. Turnbull, "Crystal Nucleation in Pd-Si Alloys", in "Materials Processing in the Reduced Gravity Environment of Space", ed. G.E. Rindone, North Holland, Amsterdam, (1982) p. 81.

2. C.V. Thompson and F. Spaepen, "The Effect of Solute on the Homogeneous Crystal Nucleation Frequency in Metallic Melts", in "Materials Processing in the Reduced Gravity Environment of Space", ed. G.E. Rindone, North Holland, Amsterdam, (1982) p. 603.

3. C.V. Thompson, A.L. Greer and A.J. Drehman, "Crystal Nucleation in Easy Glass Forming Alloys", Proc. 4th Int. Conf. Rapidly Quenched Metals, Vol. 1, ed. T. Masumoto and K. Suzuki, Jap Inst. Metals, (1982) p. 743

4. A.J. Drehman, A.L. Greer and D. Turnbull, "The Bulk Formation of a Metallic Glass: $Pd_{40}Ni_{40}P_{20}$", Appl. Phys. Lett., in press.

5. C.V. Thompson and F. Spaepen, "Homogeneous Crystal Nucleation in Binary Metallic Melts", to be published.

6. K.F. Kelton, A.L. Greer and C.V. Thompson, "Transient Nucleation in Condensed Systems", to be published.

THESIS COMPLETED:

C.V. Thompson, "Crystal Nucleation in Easy Glass-Forming Metallic Alloys", December 1981.

Paper to appear in Applied Physics Letters

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THE BULK FORMATION OF A METALLIC GLASS: $Pd_{40}Ni_{40}P_{20}$

A.J. Drehman, A.L. Greer and D. Turnbull
Division of Applied Sciences
Harvard University, Cambridge, MA 02138

Molten spheroids of $Pd_{40}Ni_{40}P_{20}$, of up to 0.53 cm minor diameter, were slowly cooled (1.4 K/sec) on a fused silica surface under 10^{-6} torr vacuum to a form which was entirely glassy except for some superficial crystallinity comprising less than 0.5% of the volume. The occurrence of crystallization was eliminated by subjecting the specimens to surface etching followed by a succession of heating and cooling cycles. The absence of crystallization in the bulk was confirmed by X-ray diffraction, transmission electron microscopy and calorimetry. Using the last technique, the heat of crystallization of the glass was measured to be 5.3 ± 0.3 kJ/g-atom.

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Normally, high cooling rates (10^2 to 10^6 K/sec) are required to quench a molten metallic alloy through its rapid crystallization regime to form a glass. For most alloys it is not clear whether the crystallization which occurs during a slower quench is the result of homogeneous or heterogeneous nucleation, although in some alloys[1,2] it appears that nucleation was homogeneous. If heterogeneous nucleation is avoided (which is in principle possible) then the minimum cooling rate required for glass formation is determined by the homogeneous nucleation rate (nuclei formed/cm^3-sec) of the alloy. From classical nucleation theory,[3] it is expected that alloys with high glass transition temperatures, T_g, relative to their equilibrium melting temperatures, T_m, will have relatively low homogeneous nucleation rates. The reduced glass transition temperature is defined by $T_{rg} = T_g/T_m$. In $Pd_{82}Si_{18}$ alloy (T_{rg} = 0.60) the homogeneous nucleation rate is quite low, less than $10^5/cm^3$-sec, and glass formation can occur at cooling rates of less than 800 K/s.[4] We decided to investigate the crystallization behavior of $Pd_{40}Ni_{40}P_{20}$ because of the possibility that this alloy, owing to is exceptionally high T_{rg} (0.67)[5] could be undercooled to bulk glass form if crystallization due to heterogeneous nucleation could be avoided.

$Pd_{40}Ni_{40}P_{20}$ alloys were prepared by RF induction melting of Ni_2P ingots (prepared from powder) and Pd strips in vacuo. The ingots were etched in a mixture of HCl and H_2O_2 to eliminate surface heterogeneities. An ingot was then inserted into the apparatus shown schematically in Fig. 1. The low part of the vessel was heated to approximately 1300 K while being evacuated to a pressure of less than 10^{-6} torr. The valve was then closed and the apparatus was disconnected from the vacuum pump and allowed to cool. After isolation from vibrations, the lower part

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was reheated (~ 1300 K) and cooled again. Successive heating-cooling cycles could be performed in this manner. A thermocouple placed within 1/2 mm of the ingot indicated the temperature during cooling (± 2 K).

Two cooling profiles are given in Fig. 2. Profile A shows an example of the occurrence of crystallization in the undercooled melt, starting at approximately 740 K. In contrast the formation of bulk glassy $Pd_{40}Ni_{40}P_{20}$ is indicated by profile B. Although this ingot contained four crystalline inclusions, they comprised less than 0.5% of the total volume and their growth was not therefore detectable on cooling profile B. This glassy ingot, the largest formed, is shown in the scanning electron microscope image of Fig. 3. One of the inclusions is visible and appears as a slight bump on the surface.

After obtaining profile B, the ingot was cut and checked for crystallinity. Neither X-ray diffraction or calorimetry indicated any crystallinity (except for the previously mentioned crystalline inclusions). Based on differential scanning calorimetry T_g = 590 K, T_e = 880 K (eutectic melting temperature) and T_l = 985 K (liquidus temperature). The onset of crystallization upon reheating was observed at approximately 645 K for a 10 K/min heating rate and the heat of crystallization was 5.3 ± 0.3 kJ/g-atom.

Fig. 4 is an optical micrograph of the eutectic structure of the largest inclusion in the ingot. The inclusion shape as well as the orientation of the lamellae imply that growth began (nucleation occurred) on the surface and proceeded inward. The planar growth rate of the eutectic structure is estimated to be approximately 1 cm/min at 740 K, as the thermal arrest (the bump of profile A) is of about 30 seconds duration and assuming a single surface nucleation event the growth distance would be about 0.5 cm. Successive heating-cooling cycles tended to reduce the

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temperature at which nucleation occurred; profile B was obtained five cycles after profile A. The inclusions must have been nucleated at a temperature below 740 K and the growth rate, which decreases with decreasing temperature, had become so low that only 0.5% of the ingot crystallized before the decreasing temperature precluded further growth ($T < T_g$).

Several transmission electron microscopy samples were prepared from the interior of the ingot. Neither electron diffraction patterns nor dark field images gave any evidence of crystalline inclusions. The samples appeared to be glassy and homogeneous throughout. Had copious homogeneous nucleation occurred then small crystallites should have been observed. Their absence implies that a cooling rate of 1.4 K/sec (as measured at 700 K) is adequate to avoid copious homogeneous nucleation.

Heterogeneous nucleation, although not completed avoided, was minimized by surface etching and thermal cycling. Without such treatment crystallization of the bulk could not have been avoided except by rapid cooling. By eliminating or reducing the effectiveness of heterogeneous nucleation sites, it should be possible to form bulk $Pd_{40}Ni_{40}P_{20}$ metallic glass (with virtually unlimited dimensions) due to the extremely low homogeneous nucleation rate indicated by our results.

This work was supported in part by NASA under contract NAS 8-32691.

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2 A.L. Greer, Acta Met. 30, 171 (1982).

3 F. Spaepen and D. Turnbull, "Formation of Metallic Glasses", Proc. of 2nd Int. Conf. on Rapidly Quenched Metals (M.I.T. Press 1976).

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FIGURE CAPTIONS

Figure 1: Schematic diagram of apparatus used for cooling melt under vacuum.

Figure 2: Superposition of two cooling profiles: A - bulk crystallization which began at 740 K. B - formation of a glassy ingot.

Figure 3: Scanning electron microscope image of a glassy ingot. A crystalline inclusion is visible and appears as a small bump.

Figure 4: Optical micrograph of the cross-section of a crystalline inclusion showing the eutectic structure.

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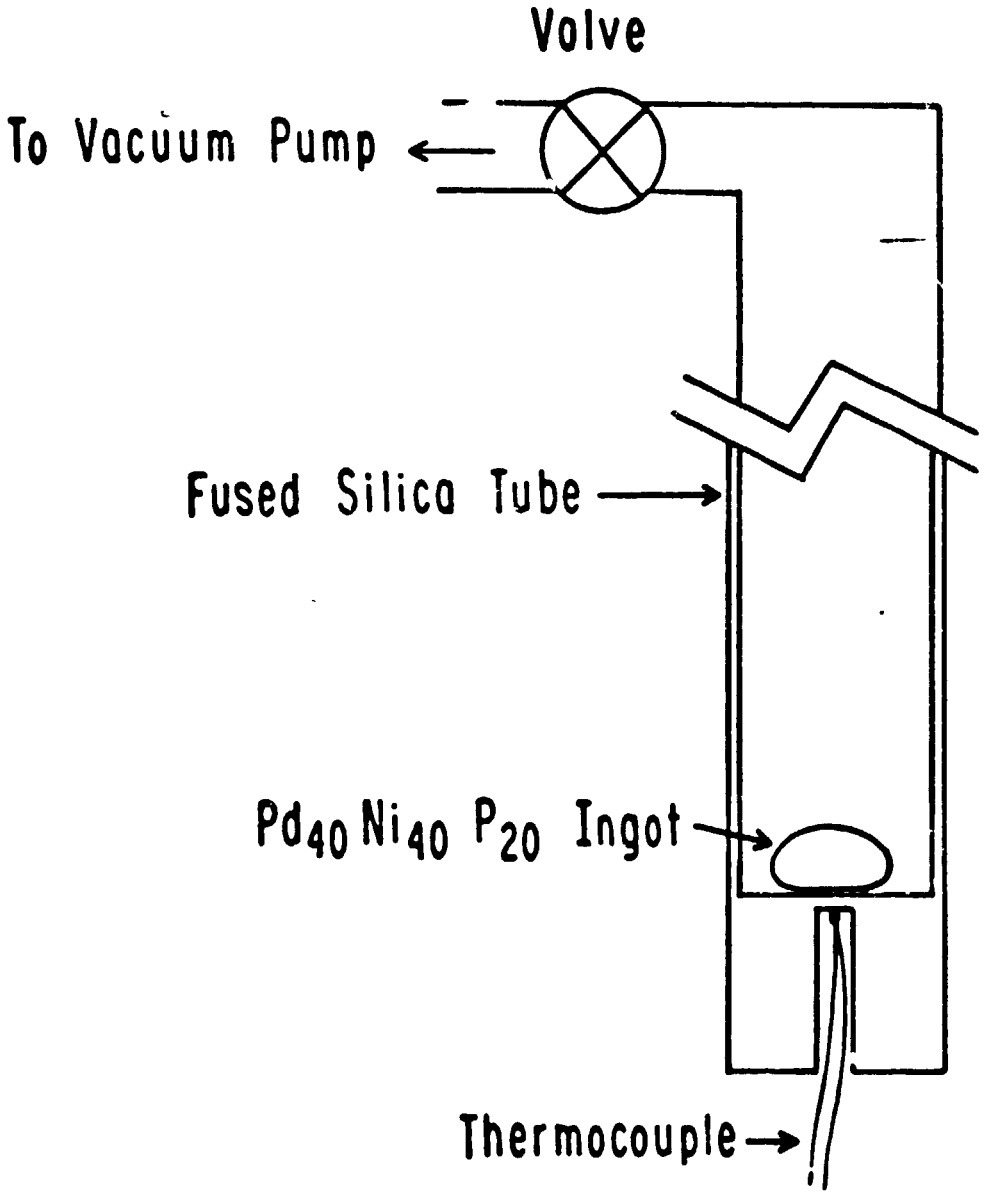

Figure 1

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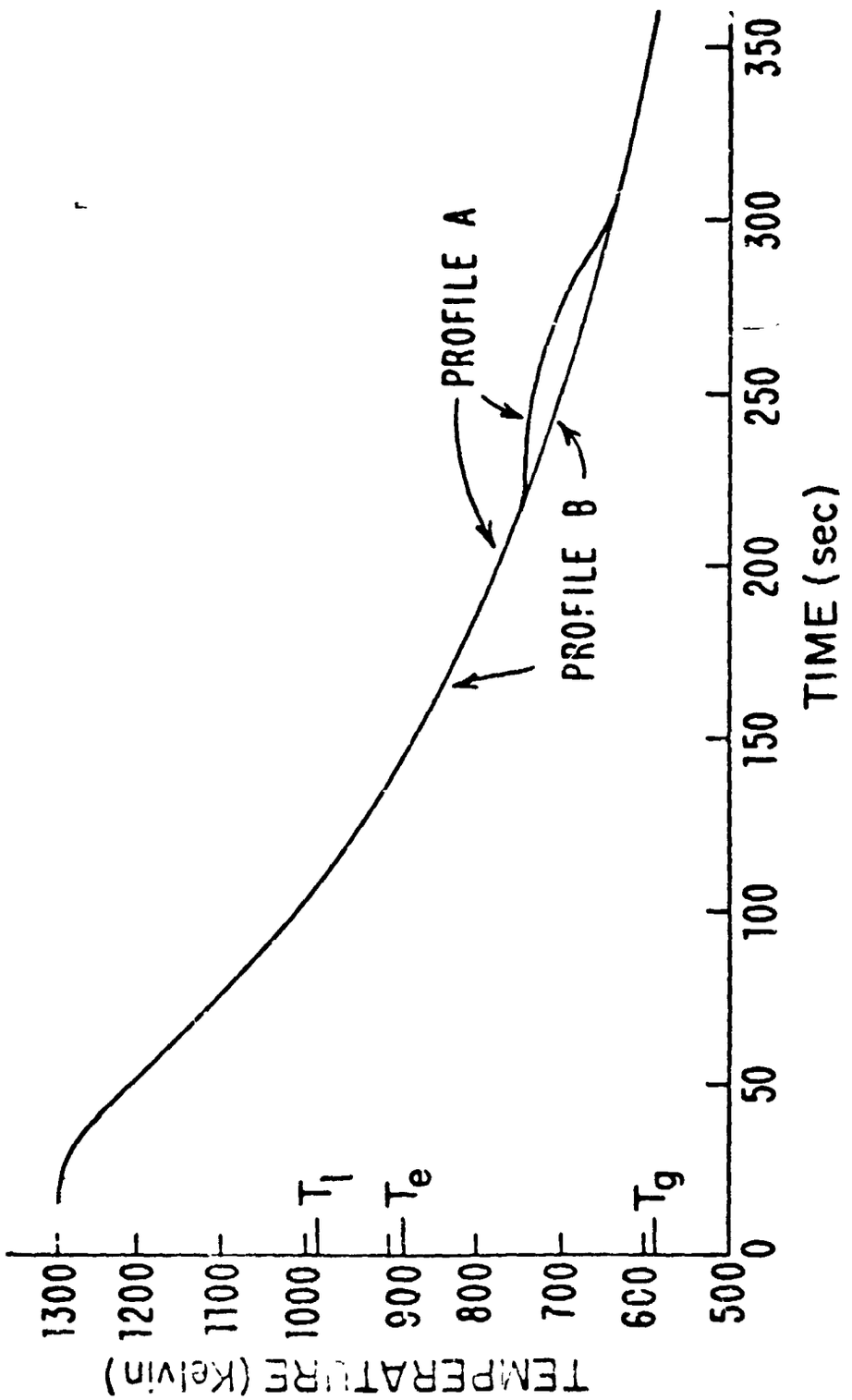

Figure 2

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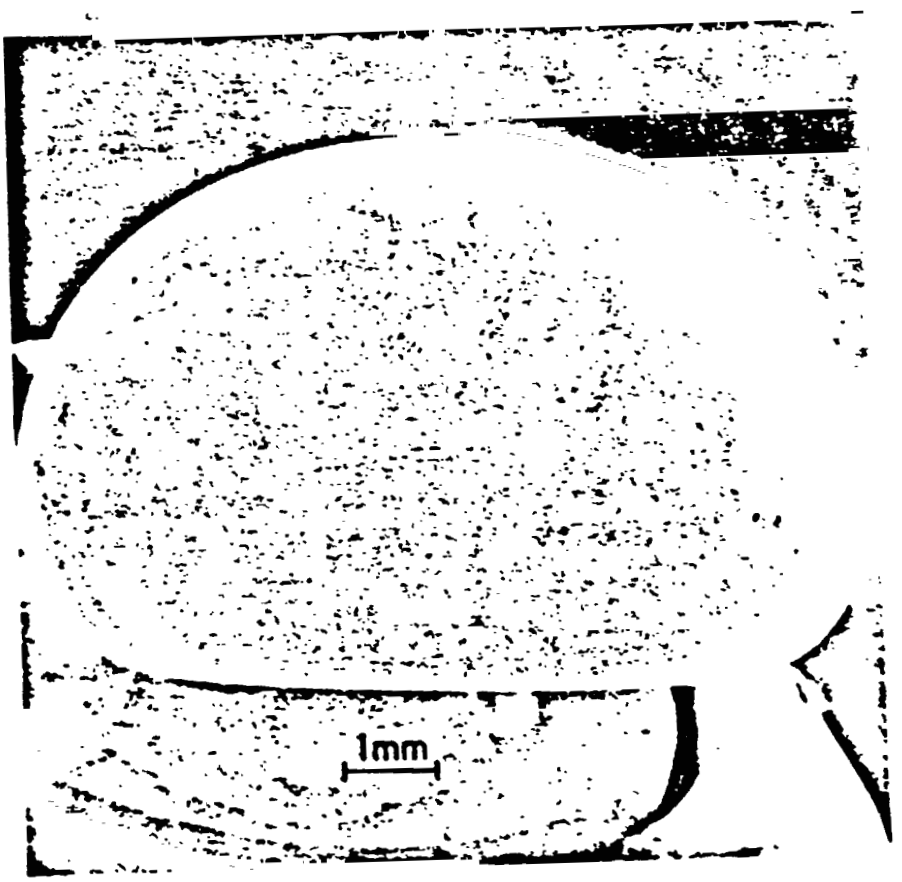

Figure 3

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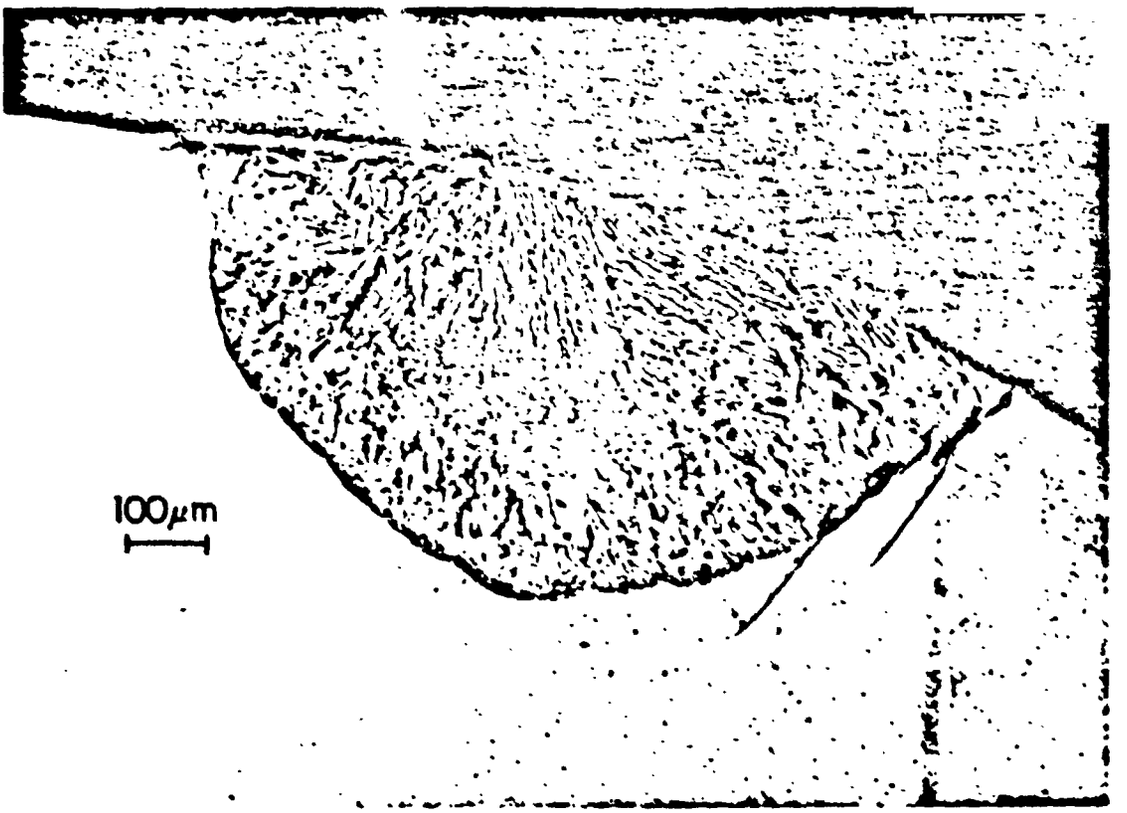

Figure 4