TABLE I Tensile properties of exemplary crystalline alloys devitrified from the glassy phase

Alloy composition (at %)	Heat-treatment	Tensile strength of heat-treated ribbon (MPa)
$Fe_{39}Cr_{25}Ni_{15}Co_{10}Mo_3W_2B_6$	850° C, 1 h	1414
$Fe_{57}Co_{10}Ni_{15}Mo_{12}B_6$	950° C, 0.5 h	1794
$Fe_{35}Cr_{25}Ni_{15}Co_{10}Mo_3W_2B_{10}$	900° C, 10 min	2242
$Ni_{44}Co_{10}Fe_{12}Cr_{18}W_5Mo_5B_6$	900° C, 0.25 h	2028
$Ni_{40}Co_{10}Fe_{10}Cr_{25}Mo_5B_{10}$	900° C, 0.25 h	1973
$Ni_{45}Co_{20}Fe_{15}Mo_{12}B_8$	900° C, 0.25 h	2173
$Ni_{57}Fe_{10}Co_{15}Mo_{12}B_6$	900° C, 0.25 h	1759
$Co_{40}Ni_{10}Fe_{10}Cr_{30}B_{10}$	900° C, 0.25 h	2277
$Co_{55}Ni_{10}Fe_{15}W_6Mo_6B_8$	900° C, 0.25 h	1980

glassy phase having a critically balanced compositions.

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References

1. J. J. GILMAN and H. J. LEAMY (EDS), "Metallic Glasses" (American Society for Metals, Metals Park, Ohio, 1978).
2. B. CANTOR (ED), "Rapidly Quenched Metals III" Vol. 1 (The Metals Society, London, 1978).
3. B. CANTOR (ED), "Rapidly Quenched Metals III" Vol. 2 (The Metals Society, London, 1978).
4. H. CHANG and S. SASTRI, *Met. Trans.* 8A (1977) 1063.
5. R. RAY, Patent pending assigned to Allied Chemical Corporation, Morristown, New Jersey.
6. R. RAY, unpublished work.
7. S. KAVESH, "Metallic Glasses", edited by J. J. Gilman and H. J. Leamy, (American Society for Metals, Metals Park, Ohio, 1978).

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Devitrification/hot consolidation of metallic glass: a new materials technology via rapid solidification processing

In the current state of the art of rapid solidification processing (RSP) technology [1–3], large scale fabrication of metallic glasses (amorphous metals) is limited to thin bodies only, e.g. ribbons, filaments, powders, etc.; hence, the technological scope of metallic glasses has failed to expand very far. Furthermore, on heating even to low temperatures, e.g. 400 to 500° C, metallic glasses based on Fe, Ni or Co devitrify to form very brittle, crystalline materials [4], and to date, few or no efforts have been made to develop applications of these brittle devitrified materials.

In a companion article [5] the author has reported the finding of a novel class of metallic glasses based on Fe, Ni and/or Co which upon heat treatment at a temperature sufficiently above the crystallization temperature (T_c) of the glassy phase become transformed into fully devitrified, multiphase, microcrystalline alloys having high tensile strength, good ductility and excellent thermal stability.

The aforementioned glasses are characterized by certain critical contents of transition metals and metalloids. The total content of metalloids e.g. B, P, C and Si in these alloys ranges between 5 and 13 at%; boron is the dominating metalloid element in these alloys.

It is possible to consolidate the metallic glass alloys of the present work, in a form such as ribbon or powder, by suitable thermomechanical processing techniques under simultaneous application of pressure and heat at temperatures between

0.6 and 0.95 of the solidus temperatures (T_s) into fully-dense three-dimensional structural parts of any suitable geometric form. The consolidated parts can be given additional thermal and/or thermomechanical treatment to achieve optimum microstructure and mechanical properties. Such consolidated products may have numerous high strength engineering applications, both at room temperature and at elevated temperatures.

Employment of temperatures outside the above ranges leads to undesirable results. At temperatures below about 0.6 T_s, the kinetics of transformation of glassy phase to optimum microcrystalline microstructures are extremely sluggish and even after indefinitely long anealing times beyond 100 h, the devitrified alloys tend to remain brittle and weak. From a practical standpoint, the heat-treatment process is inefficient at temperatures below about 0.6 T_s. Moreover, if hot-work processing (i.e. hot extrusion, hot pressing, etc.) of the above glassy alloys is attempted below 0.6 T_s to consolidate them into fully dense bulk-shape devitrified parts, complete sintering will not be achieved and a fully dense compact cannot be obtained. At temperature above about 0.95 T_s, the heat treatment time which would result in the desired microstructure is impractically short.

A number of selected metallic glasses of the present finding were converted into fully dense bulk, devitrified crystalline objects, i.e. bar, disc, ingot etc. by hot consolidation (i.e. hot extrusion or hot isostatic pressing) of glassy powders. Metallic glass powders were prepared by pulverization of glassy ribbons. The melt-spinning pulverization procedure for preparing glassy powders is preferred over other known RSP powder processes, e.g. melt-atomization techniques [6, 7]. In atomization techniques, the quench rate (and hence the metastable structure and the final, heat-treated structure derived thereform) varies greatly with particle size. In powders made by pulverization of melt spun ribbons, particles of all sizes have experienced essentially the same quench history.

The following examples illustrate production of devitrified crystalline rods by the method of hot extrusion of iron-base metallic glass alloy powders. About 5 kg of powder of each different glassy alloy with particle size under 100 mesh were packed in 8 cm O.D. mild steel cans, sealed under vacuum. The cans were heated at 950° C for 2.5 h and extruded into 2.5 cm diameter rods. The extruded rods were tested for tensile strength and the results are given in Table I.

The following example illustrates the production of a devitrified crystalline rod by thermomechanical processing of thin metallic glass ribbons. About 5 kg of 2.5 to 1.5 cm wide metallic glass ribbons having a composition $Fe_{63}Cr_{12}Ni_{10}Mo_3B_{12}$ were tightly wound in 8 cm diameter rolls. The rolls were stacked in a mild steel can and sealed under vacuum. The can was heated at 950° C for 2.5 h and hot-extruded into a fully-dense 3 cm diameter rod. The extruded rod was found to have ultimate tensile strength of 1379 MPa, 5.1% elongation and 7.1% reduction in area at room temperature.

The devitrified iron-based alloys containing chromium and/or refractory metals, Mo, W etc. in consolidated form possess excellent oxidation resistance and/or high hot strength/hardness at intermediate high temperatures in the range 540 to 650° C.

A metallic glass alloy having a composition $Fe_{70}Cr_{18}Mo_2B_{10}$ (at%) was made into powder with a particle size less than 80 mesh (US). The powder was hot extruded after heating at 950° C for 2 h in an evacuated sealed can, to obtain a fully dense, devitrified rod. The devitrified crystalline alloy was found to have excellent high-temperature stability of mechanical properties up to 540° C, as illustrated in Table II.

A metallic glass alloy having the composition $Fe_{70}Cr_{18}Mo_2B_9Si_1$ (at%) was made into powder (−80 mesh US). The powder was put in a mild steel can, evacuated, sealed off and subsequently hot-extruded after heating at 950° C for 2 h with an extrusion ratio of 9 to 1. The hardness of a sample for the extruded rod was tested from room temperature to 650° C. The devitrified material

TABLE I Room-temperature tensile properties of crystalline iron-base alloys hot-extruded from glassy powders

Composition (at%)	Ultimate tensile strength (MPa)
$Fe_{70}Cr_{18}Mo_2B_{10}$	1504
$Fe_{70}Cr_{13}Ni_6Mo_1B_9Si_1$	1577
$Fe_{63.5}Cr_{14.5}Ni_{10}Mo_2B_{10}$	1535
$Fe_{62.5}Cr_{16}Mo_{11.5}B_{10}$	1573
$Fe_{63.5}Cr_{15}Mo_{11.5}B_8Si_2$	1439

TABLE II Tensile properties of a devitrified crystalline iron-base alloy $Fe_{70}Cr_{18}Mo_2B_{10}$ hot-extruded from glassy powders

Temperature (°C)	Ultimate tensile strength (MPa)
108	1504
324	1517
432	1517
540	1276

was found to have excellent resistance to softening at elevated temperatures up to 650° C (see Table III).

A metallic glass alloy having the composition $Fe_{63}Cr_{22}Ni_3Mo_2B_8C_2$ was made into powder with a particle size less than 80 mesh. The powder was hot extruded in an evacuated can at 1050° C into a fully dense devitrified body. The corrosion behaviour of the devitrified, consolidated bodies was studied and compared with that of Type 304 and Type 316 stainless steel. The results indicate that the corrosion rate of the devitrified alloy is about one-tenth of that of 304 and 316 stainless steels in 1N sulphuric acid at room temperature.

The devitrified alloys containing small additions of carbon such as

$$Fe_{75}Cr_{10}Mo_5B_8C_2,$$

$$Fe_{78.5}Cr_5V_2Mo_2W_2B_{7.5}C_{2.5}Si_{0.5}$$

and

$$Fe_{78}Cr_5W_7B_8C_1Si_1$$

(subscripts are in atom per cent) have the capability of responding to heat treatment in order to change their hardness and ductility, analogous to the manner in which hardness and ductility of steel may be changed by heat treatment (i.e. hardening, tempering, annealing, etc.). Hardness values in excess of Rockwell C 68 can be achieved in these alloys by suitable heat treatment procedures. High hardness values of these boron–carbon containing alloys are believed to be due to the unique microstructures consisting of *martensite* and ultra-fine borides.

TABLE III Hot hardness values of a devitrified crystalline iron-base alloy $Fe_{70}Cr_{18}Mo_2B_2Si_1$ (at%) hot-extruded from glassy powder

Temperature	Hardness (Rockwell C)
Room temperature	44
324	43
432	43
540	43
648	42.5

Exemplary preferred alloys of the above category include those having the composition (atom per cent)

$$Fe_{bal.}Cr_{5-10}V_{1-3}W_{3-5}Mo_{3-7}B_{7-8}C_{2-2.75}Si_{0.5-1}.$$

These alloys can be devitrified/hot consolidated in bulk forms from the corresponding glassy state (powders). By suitable heat treatment, the devitrified alloys can be subsequently rendered readily machineable into any desired form, e.g. cutting tools. Thereafter, the machined parts can be heat treated to give the desired properties having excellent durability.

From the discussion of the above results and those reported in the previous communication, it is clearly evident that for a wide spectrum of structural/engineering applications, the bulk, devitrified, crystalline alloys designed and processed to have the optimum microstructures and properties might pose serious threats to the viability of many commercial alloys, e.g. common stainless steels, precipitation hardenable stainless steels, hot-work tool steels, high-speed cutting steels, etc.

In the author's opinion, the results reported here may very well serve as a basis for a viable *new materials technology*, i.e. "bulk, devitrified, crystalline materials with useful engineering properties prepared from metallic glasses". The technology of bulk devitrified materials can advance rapidly taking full advantages of the vital fabricating principles involved, i.e. melt-spinning, pulverization and powder-metallurgical consolidation, which are all well known techniques.

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References

1. J. J. GILMAN and H. J. LEAMY (EDS), "Metallic Glasses" (American Society for Metals, Metals Park, Ohio, 1978).
2. B. CANTOR (ED), "Rapidly Quenched Metals III" Vol. 1 (The Metals Society, London, 1978).
3. B. CANTOR (ED), "Rapidly Quenched Metals III" Vol. 2 (The Metals Society, London, 1978).

4. H. CHANG and S. SASTRI, *Met. Trans.* 8A (1977) 1063.
5. R. RAY, Patent pending assigned to Allied Chemical Corporation, Morristown NJ, USA, and *J. Mater. Sci.* 16 (1981) 2924.
6. M. R. GLICKSTEIN, R. J. PATTERSON II and N. E. SHOCKEY, "Rapid Solidification Processing", edited by R. Mehrabian, B. H. Kear and M. Cohen (Claitor's Publishing Division, Baton Rouge, Louisiana, 1978).
7. N. J. GRANT, "Rapid Solidification Processing", edited by R. Mehrabian, B. H. Kear and M. Cohen (Claitor's Publishing Division, Baton Rouge, Louisiana, 1978).

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The preparation and characteristics of ZrC and TaC single crystals using an r.f. floating-zone process

TaC exhibiting superconductivity has the highest melting point (~ 3900° C) of the refractory carbides, hence, its single crystal has not been obtained using the radio frequency (r.f.) floating-zone process [1]. In contrast, the authors have grown comparatively large single crystals of TaC by the r.f. floating-zone process. Prior to growing TaC crystals the preparation of ZrC single crystals was attempted. The method of preparation was based on the knowledge that single crystals of NbC with nearly the same melting point at ZrC, have previously been grown using an r.f. generator of 30 kW [2], but it was impossible to obtain ZrC single crystals using this method. By contrast, an r.f. generator of 50 kW made it possible to grow large ZrC single crystals easily. The present note describes the preparation and characteristics of ZrC and TaC single crystals grown by the r.f. floating-zone process at a pressure of 10 atm.

The operating procedures for growing crystals were essentially the same as those previously described for TiC [3] and NbC [2]. The working coil for ZrC was a six- or eight-turn co-planar coil of water-cooled copper tubing, while for TaC an eight-turn co-planar coil was used. The growth of TaC single crystals is far more difficult than ZrC. About 1 h after the formation of the molten zone of TaC, the crack initiated at the surface of the specimen, but it was possible to observe the molten material through the crack. The fundamental difficulties in growing TaC single crystals result from the surface tension not being sufficiently high to maintain a zone with a high density (14.5 g cm^{-3}). Also the coils are punctured by arcing between the coil and melt.

Metallic-looking ZrC single crystals 8 mm in diameter and 60 mm long were grown. A typical example is shown in Fig. 1. Fig. 2 shows the TaC single crystal appearing at the cleavage planes. Except for the surface of the crystal, which was a golden yellow colour, it had a silver metallic look. There was a longitudinal crack. The macrophotographic observation of the cross-section along the dotted line in Fig. 2a is shown in Fig. 2b. There appears to be a large melted grain and a cleavaged crack. ZrC was greater than 99.9% pure and TaC was 99.5% pure as determined by X-ray fluorescence analysis. The average chemical composition was $ZrC_{0.9}$ and $TaC_{0.83}$ as obtained by chemical analysis and electron microprobe X-ray analysis. X-ray powder diffraction patterns of crushed specimens indicate a lattice parameter of $a_0 = 0.4702$ and 0.4429 nm for ZrC and TaC, respectively. The growth direction almost coincided with the $\langle 110 \rangle$ or $\langle 100 \rangle$ direction in ZrC and the $\langle 110 \rangle$ direction in TaC. Dislocation pits of ZrC

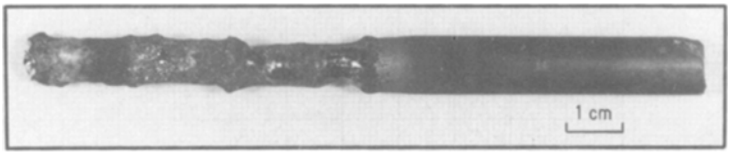

Figure 1 As-grown single crystal of ZrC.

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