

is in excellent agreement with the spacing of the reflections measured from the diffraction pattern and so it can be assumed that the (010) lattice planes have been successfully imaged in pDCH single crystals.

It is worth considering the reasons why direct lattice resolution is possible in pDCH crystals. The main reason appears to be that pDCH is very resistant to beam damage. Although quantitative measurements have not yet been made it is thought that they are a factor of two or three times more resistant than pTS and they appear to have approximately the same stability as the copper phthalocyanine standards. Also, the fibrous crystals have a roughly hexagonal cross-section and so they tend to lie on the substrate in a variety of orientations. Inspection of the crystal structure of pDCH in the paper of Enkelmann *et al.* [14] shows that when the crystal is viewed along the *a*-axis (unconventionally indexed) the (010) planes appear as widely-spaced stacks of molecules. The presence of these stacks in this orientation probably helps to obtain a good periodic image [1]. In pTS the crystals tend to adopt a lamellar habit [7] with a surface normal of approximately [120]. In this orientation the stacks of molecules are off-set from each other.

It is clear that the ability to obtain lattice images from polydiacetylene single crystals should enable considerable progress to be made in the understanding of the structure and properties of polymer crystals. In particular it is intended to use the technique to study the structure of defects such as dislocations, stacking faults, grain boundaries and twins in these materials.

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High strength microcrystalline alloys prepared by devitrification of metallic glass

Metallic glasses (amorphous metals) are conveniently prepared by rapid quenching from the melt of certain glass-forming alloys [1–3]. This requires quench rates of the order of 10^5 to 10^6 °C sec⁻¹ or higher. Such quench rates are obtained by depositing molten metal in a thin layer onto a heat

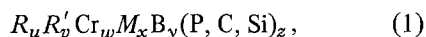
extracting member, such as a block of copper. Known methods for doing this include splat quenching, hammer-and-anvil quenching, as well as the melt-spin procedures. However, in all of these procedures, the quenched glassy metal product must have at least one small dimension, usually less than 0.1 mm thick. Glassy metals obtained by the melt-quench procedure, therefore, are limited to powders, thin wires and thin filaments such as

strip or sheet. Many metallic glasses have outstanding properties such as high hardness, high strength, corrosion resistance and/or magnetic properties. However, the thinness of the bodies in which metallic glasses are obtained by melt-quench procedures has in the past limited their use. Also, on heating to even moderately low temperatures, metallic glasses will devitrify to form extremely brittle, crystalline materials [4] and to date no outstanding uses for such crystalline materials have been developed.

In a recent research programme, the present author successfully synthesized a novel class of metallic glasses based on Fe, Ni and/or Co which upon heat treatment at temperatures sufficiently above the crystallization temperature (T_c) of the glassy phase become transformed into fully devitrified, crystalline multiphase alloys having high tensile strength, good ductility and excellent thermal stability [5].

One novel group of ferrous metallic glasses formulated with certain critical combinations of transition metals and metalloids are briefly reported herein. A detailed description of this investigation describing other alloy groups will be published later [6].

The aforesaid glass-forming alloys have compositions with the formula



where R is one of iron, cobalt or nickel; R' is one or two of iron, cobalt or nickel other than R ; Cr , B , P , C and Si , respectively, represent chromium, boron, phosphorus, carbon and silicon; M is one or more of molybdenum, tungsten, vanadium, niobium, titanium, tantalum, aluminum, tin, germanium, antimony, beryllium, zirconium, manganese and copper; u , v , w , x , y and z represent atom per cent of R , R' , Cr , M , B and (P, C, Si) , respectively and have the following values: $u = 30-85$; $v = 0-30$; $w = 0-45$; $x = 0-30$; $y = 5-12$ and $z = 0-7.5$, with the provisos that (1) the sum of $v + w + x$ is at least 5; (2) when x is larger than 20, then w must be less than 20; (3) the amount of each of vanadium, manganese, copper, tin, germanium, antimony and magnesium may not exceed 10 at%; and (4) the combined amount of boron, phosphorus, carbon and silicon may not exceed about 13 at%.

Metallic glass ribbons (prepared by standard

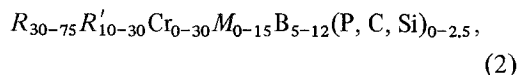
melt spinning techniques [7]) of the aforesaid composition, when heated to temperatures from about 0.6 to about 0.95 of the solidus temperature, T_s but above the crystallization temperature, T_c , of the metallic glass composition, are converted into a devitrified, crystalline, ductile precipitation-hardened multiphase alloy having high tensile strength, generally of at least about 1242 MPa and high hardness.

The required heating time depends upon the temperature used and may range from about 0.01 to about 100 h, more usually from about 0.1 to about 1 h, with higher temperatures requiring shorter heating times.

The most preferred heat-treatment procedure used to obtain the highest tensile strength value involves heating the glassy alloys of Formula 1 to a temperature within the range of about $0.7 T_s$ to about $0.8 T_s$ for a period of about 0.5 to about 10 h.

Addition of refractory metals, such as Mo, W, Nb or Ta up to about 30 at%, preferably up to about 20 at% and/or of chromium up to 45 at% in the alloys generally improves the physical properties (strength, hardness) as well as the thermal stability and/or oxidation and corrosion resistance of the crystalline alloys. Alloy compositions of Formula 1, above, containing from about 1 to 15 at% of one or more of Mo, W, Nb, Ta, more desirably of Mo and/or W, are a preferred class of alloys.

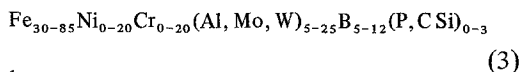
A preferred type of metallic glasses within the scope of Formula 1 which can be converted by heat-treatment into devitrified, crystalline alloys having high tensile strength and high thermal stability are alloys having the composition (in atom per cent) of the formula



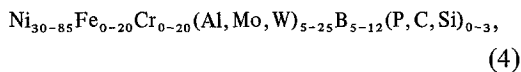
where R is one of the elements of the group consisting of Fe, Ni and Co; R' is one or two elements of the group consisting of Fe, Ni and Co other than R ; M is an element of the group consisting of Mo, W, Nb and Ta. and where the sum of Cr , R' and M must be at least 12 at%. The boron content is 80 at% or more of the combined metalloid content (B, P, C and Si) in the alloy. Exemplary preferred alloy compositions of Formula 2 include:

$Fe_{40}Ni_{10}Co_{10}Cr_{30}B_{10}$, $Fe_{50}Cr_{25}Ni_{10}Mo_5B_{10}$,
 $Fe_{39}Cr_{25}Ni_{15}Co_{10}Mo_3W_2B_6$, $Fe_{45}Cr_{20}Ni_{15}Mo_{12}B_8$,
 $Ni_{39}Cr_{25}Fe_{15}Co_{10}Mo_3W_2B_6$, $Ni_{57}Fe_{10}Co_{15}W_6Ta_6B_6$,
 $Co_{55}Fe_{15}Ni_{16}W_6B_8$ and $Co_{65}Fe_{10}Ni_{10}Mo_7B_8$.

Another preferred type of metallic glass within the broad composition range of Formula 1 which can be converted by heat-treatment into devitrified crystalline alloys having high tensile strength and high thermal stability, and excellent oxidation resistance at elevated temperatures, are iron and nickel based alloys containing at least 5 at% of aluminium having the formulae



and

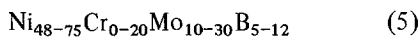


where the combined content of Al, Cr, Mo and/or W cannot be less than 10 at%; the combined content of Mo and W cannot be more than 5 at%, and the maximum combined content of metalloid elements may not exceed 12 at%. Exemplary preferred alloy compositions of the above Formulae 3 and 4 include

$Fe_{70}Cr_{15}Al_5B_{10}$, $Fe_{60}Cr_{20}Al_{10}B_{10}$, $Fe_{65}Cr_{15}Al_{10}B_{10}$,
 $Fe_{60}Cr_{15}Al_{10}Mo_5B_{10}$, $Fe_{60}Cr_{15}Al_{15}B_{10}$ and
 $Ni_{60}Cr_{10}Al_{20}B_{10}$.

Glassy bodies e.g. ribbons of alloys of Formulae 3 and 4, when heat-treated in accordance with the method of this work at temperatures in the range 800 to 950°C for 10 min to 3 h are converted into ductile crystalline bodies, e.g. ribbons. Hardness values of these devitrified bodies may vary from 450 to 1000 kg mm⁻² depending on alloy composition and heat-treatment cycle.

Yet another type of metallic glass which can be converted by heat-treatment, as described here, into devitrified crystalline alloys having high tensile strength and high thermal stability are nickel-based compositions having the formula



in which, when Mo is larger than 20 at%, Cr must be equal or less than 15 at%. Alloys of the above formula have excellent mechanical properties at elevated temperatures. Exemplary alloys of the above category include: $Ni_{55}Cr_{15}Mo_{20}B_{10}$, $Ni_{65}Mo_{25}B_{10}$, $Ni_{60}Mo_{30}B_{10}$, $Ni_{62}Cr_{10}Mo_{20}B_8$ and $Ni_{57}Cr_{10}Mo_{25}B_8$.

Glassy bodies, e.g. ribbons of alloys of Formula 5, when heat-treated, say, at temperatures between 900 and 1050°C for 2 to 6 h, are converted into ductile crystalline bodies, e.g. ribbons. The hardness of these devitrified bodies may vary from 600 to 1000 kg mm⁻² depending on alloy composition and heat treatment cycle.

Several other preferred types of metallic glasses synthesized as subgroups of the general class of alloys of Formula 1 will be reported in a future publication [6].

A number of iron, nickel and cobalt base fully glassy ribbons containing from about 5 to 12 at% boron of composition within the scope of Formula 1 were heat-treated/devitrified above their crystallization temperatures. The ribbons were heat treated under vacuum of 10⁻² torr at a temperature between 850 and 950°C for periods of about 10 min to 1 h. The above heat-treatment temperatures corresponded to 0.7 to 0.8 of the absolute solidus temperature of the alloys in the present investigation. The heat-treated ribbons were found, by X-ray diffraction analysis, to be 100% crystalline phases. The heat-treated ribbons were found to be ductile to 180° bending, which corresponds to a radius of zero in the bending test. The hardness values of the devitrified ribbons ranged between 670 and 750 kg mm⁻².

The devitrified ribbons having alloy compositions used in present research possess remarkable thermal stability at elevated temperatures.

Metallic glasses having compositions, $Ni_{40}Co_{10}Fe_{10}Cr_{25}Mo_5B_{10}$ and $Fe_{40}Cr_{30}Ni_{10}Co_{10}B_{10}$ were crystallized at 950 and 900°C, followed by isothermal annealing at 700°C. No change in hardness was observed on ageing up to 200 h at 700°C.

Ultimate tensile strength of some of the devitrified, crystalline ribbons was measured on an Instron machine using ribbon with unpolished edges. The results of tensile tests are given in Table I.

Transmission electron microscopy examination of a few selected alloys in the fully ductile, devitrified state shows the microstructure consisting of a uniform dispersion of ultra-fine boride particles in a microcrystalline (ultra-fine grained) matrix.

The excellent physical properties of the devitrified alloys are believed to be due to unique microstructure obtained via crystallization under specific thermal conditions of a single, isotropic

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 ₃ W ₂ B 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 ₃ W ₂ B ₁₀	900° C, 10 min	2242
Ni ₄₄ Co ₁₀ Fe ₁₂ Cr ₁₈ W ₅ Mo ₅ B ₆	900° C, 0.25 h	2028
Ni ₄₀ Co ₁₀ Fe ₁₀ Cr ₂₅ Mo ₅ B 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 ₆ Mo ₆ B ₈	900° C, 0.25 h	1980

glassy phase having a critically balanced compositions.

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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, multi-phase, 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