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# Performance Advances in **Copper-Nickel-Tin Spinodal Alloys**

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**The unique metallurgy and microstructure of Cu-Ni-Sn alloys offer a beneficial combination of strength, tribology, corrosion resistance, toughness, and reliability for diverse applications in the oil and gas, aerospace, mechanical systems, and electronics industries.**

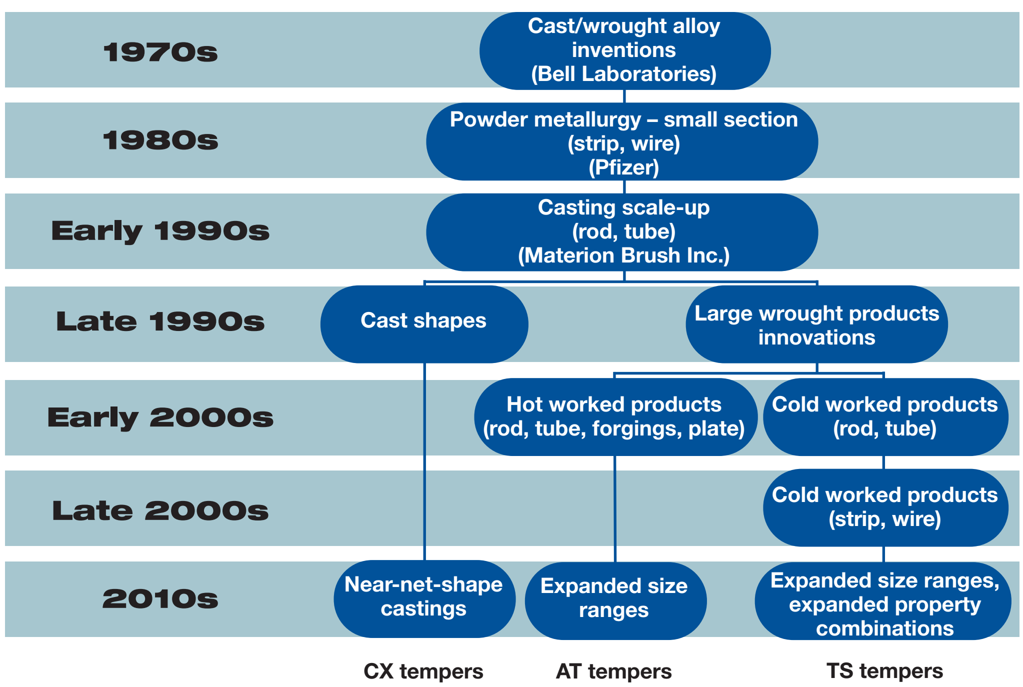
Scientists have known about spinodal materials for some time, but it was not until J. Willard Gibbs first identified the thermodynamic stability associated with spinodal decomposition that ceramic scientists began to explore their possibilities in the first half of the 1900s. Researchers continued to explore metallic systems in the latter part of the 20th century, but it was not until the 1960s that detailed alloy imaging was realized using transmission electron microscopy.

Bell Laboratories exploited Cu-Ni-Sn alloys in the late 1960s, developing innovations and patents in the 1970s. However, commercialization of wrought Cu-15Ni-8Sn alloy was limited and eventually abandoned due to hot cracking during traditional hot rolling or forging. Although powder metallurgy made the system viable in the 1980s for low cross-section products such as strip and wire, it was not until the early 1990s that casting technology evolved to solve the hot working problem associated with larger section product forms. See Table 1.

Materion Brush Inc. achieved a breakthrough in the 1990s after constructing a plant dedicated to a new casting process to produce the EquaCast microstructure, followed by extensive development of hot working technology. The company now casts and hot works sections as large as 24-in. in diameter to produce significant sizes of bar, tube, plate, and strip, and development of cold worked tempers of all product forms is emerging.

Materion developed and commercialized Cu-Ni-Sn alloys using lean sigma methodology and tools. End-user needs were broken down into project packages and a series of projects helped to expand the alloy family by

**TABLE 1 — EVOLUTION OF COPPER NICKEL TIN SPINODAL ALLOYS**

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This article updates the current state of the art regarding Cu-15Ni-8Sn alloy manufactured under the tradename ToughMet 3, which uses vertical continuous casting and molten metal stirring to produce the so-called EquaCast microstructure. This casting technology enables hot working processes, extending the property combination options that meet demanding application needs in aerospace bearings, oil and gas exploration components, tribologic parts for mechanical systems and machinery, and electronic connectors. An article in the June 2006 edition of *Advanced Materials & Processes* provides more detail about the metallurgy and utility of ToughMet 3. Selected references further detail the alloy system.

further developing and verifying process reliability. Using production material, engineers were able to verify property sets. Production lots were separated by both time and dimension to measure within and between variation in the system. These results were valuable for developing manufacturing control plans as alloy tempers were commercialized. In addition, this approach helped significantly when introducing the alloy into the materials community.

## Spinodal alloy metallurgy

Most copper-base alloys derive strength from solid solution hardening, cold working, precipitation hardening, or a combination of these. In the ternary copper-nickel-tin alloys that include Cu-9Ni-6Sn (ToughMet 2) and Cu-15Ni-8Sn (ToughMet 3), the high mechanical strength options shown in Table 2 are produced by controlled thermal treatment that causes spinodal decomposition.

Classic spinodal decomposition takes place spontaneously and does not require an incubation period. Instead of the typical nucleation-and-growth process, spinodal decomposition is a continuous diffusion process in which the original alloy decomposes into two chemically different phases with identical crystal structures. Each phase in the spinodally hardened alloy is on the nanoscale and is continuous throughout the grains up to the grain boundaries.

Spinodal decomposition in copper-nickel-tin alloys triples the yield strength of the base metal and results from the coherency strains produced by the uniform and high-number-density dispersion of tin-rich perturbations in the copper matrix. Cold working prior to the spinodal hardening treatment adds additional strength and ductility.

Spinodal decomposition hardening only happens under certain conditions—the solid-state phase diagram of a spinodal system must contain a miscibility gap, a region in which the single phase alloy separates into nanophases. The alloying elements must also have sufficient mobility in the parent matrix at the miscibility gap to allow interdiffusion.

## Spinodal heat treatment

Heat treatment steps for spinodal decomposition include:

**TABLE 2 — PROPERTIES OF COPPER NICKEL TIN SPINODAL ALLOY PRODUCTS**

| Alloy | Description | Specifications and MMPDS handbook appearances | 0.2% Offset yield strength | Tensile strength | Tensile elongation | Hardness | CVN impact strength | $K_{Ic}$ fracture toughness | Product forms |
|---|---|---|---|---|---|---|---|---|---|
| UNS C96970<br>ToughMet 2 CX | Cast and spinodally hardened | — | 90-100 ksi<br>620-690 MPa | 105-110 ksi<br>725-760 MPa | 10-5% | HRC 27-29 | — | — | rod, tube, custom shape |
| UNS C96900<br>ToughMet 3 CX | | ASTM B505 | 95-105 ksi<br>655-725 MPa | 100-110 ksi<br>690-760 MPa | 6-4% | HRC 27-30 | — | — | |
| UNS C72900<br>ToughMet 3 AT | Wrought and spinodally hardened | AMS 4595 (plate), AMS 4596 (rod and bar), AMS 4598 (tube), ASTM B929, MMPDS-07 (rod, bar, and tube) | 90-110 ksi<br>620-760 MPa | 110-135 ksi<br>760-930 MPa | 15-4% | HRC 26-32 | 9-4 ft lb<br>12-5 J | 45-30 ksi$\sqrt{in}$<br>49-33 MPa$\sqrt{m}$ | rod, tube, plate |
| UNS 72900<br>ToughMet 3 TS | Wrought, cold worked, and spinodally hardened | AMS 4597 (rod and bar), MMPDS-07 (rod and bar) | 95-150 ksi<br>655-1035 MPa | 106-165 ksi<br>730-1140 MPa | 18-3% | HRB 97-HRC 36 | 30-4 ft lb<br>40-5 J | 70-40 ksi$\sqrt{in}$<br>77-44 MPa$\sqrt{m}$ | rod, tube, wire |
| UNS C72900<br>BrushForm 158 | | ASTM B740 | 75-200 ksi<br>515-1380 MPa | 95-205 ksi<br>655-1415 MPa | 22-1% | HRB 89-HRC 38 | — | – | strip |
| UNS C72700<br>BrushForm 96 | | ASTM B740 | 55-140 ksi<br>380-965 MPa | 90-160 ksi<br>620-1105 MPa | 16-1% | HRB 91-HRC 45 | — | — | strip |

- Homogenization at a temperature above the miscibility gap to develop a uniform solid solution of a single phase
- Rapid quenching to room temperature to retain the solid solution state
- Reheating to a temperature within the spinodal region to initiate the reaction, and holding for sufficient time to complete the spinodal decomposition

Materion's copper-nickel-tin alloys are spinodally hardened at the mill, eliminating the need for heat treatment by users. In this pre-hardened condition, alloys are fully machinable and offer unique combinations of high strength, corrosion resistance, and low friction and wear.

## Spinodal microstructure

Alloys strengthened by spinodal decomposition develop a characteristic modulated microstructure. Resolution of this fine scale structure is beyond the range of optical microscopy and is only resolvable by skillful transmission electron microscopy. Alternatively, satellite reflections around the fundamental Bragg reflections in x-ray diffraction patterns can confirm spinodal decomposition in copper-nickel-tin and other alloy systems.

Tin-rich zones formed by spinodal decomposition during early heat treatment stages develop an ordered structure in the peak-aged condition, further enhancing strength. Overaging produces a discontinuous grain boundary reaction consisting of a pearlitic $\alpha + \gamma$ phase mixture that consumes spinodally hardened grains, leaving behind a soft microstructure with reduced ductility.

## Product evolution

As shown in Table 1, product forms have become more diverse, and in general, larger during the 2000s. This stems from growing market awareness of the property combinations that can meet field service demands. More specifically, four major market segments—oil and gas, aerospace, mechanical systems, and electronics—have spurred new product development. See Table 3.

*Oil and gas*—Demands in the exploration segment of the oil and gas industry traditionally require inherent magnetic transparency, high strength, resistance to stress corrosion cracking (SCC), and antifriction characteristics of the system. Further needs for robustness during handling, make up, and in-service dynamic loading require increased impact toughness, notch strength, and fracture toughness. These requirements are being met by two new tempers with significantly higher

**TABLE 3 — DESIRED MATERIAL ATTRIBUTES**

| Market segment | Desired attribute | Influencing material properties |
|---|---|---|
| Oil & gas | Resistance to fracture | $K_{1C}$, CVN impact strength, notch strength ratio |
| Oil & gas, aerospace | Fatigue resistance | Fatigue strength, fatigue crack propagation |
| Electronic connectors | Vibration damping (stiffness) | Elastic modulus |
| Oil & gas, aerospace, mechanical systems, electronic connectors | Long life/reliability | Fatigue strength, wear resistance, corrosion resistance, stress relaxation resistance, statistical analysis of these properties |
| Oil & gas | Galling resistance | Hardness, elastic modulus |
| Mechanical systems, aerospace | Wear resistance | Work hardening rate |
| Mechanical systems, aerospace | Heat generation, power loss | Coefficient of friction |
| Mechanical systems, aerospace, oil & gas | Abrasion resistance | Yield strength, ultimate strength |
| Mechanical systems, aerospace, electronic connectors | Low operating temperature | Thermal conductivity, electrical conductivity |
| Oil & gas | Compatibility with other alloys | Galvanic potential |
| Oil & gas, electronic connectors | Temperature resistance | Elevated temperature strength, stress relaxation resistance |
| Aerospace, mechanical systems, oil & gas | Cracking/spalling resistance | Fatigue strength |
| Mechanical systems, aerospace | Interference fit stability | Stress relaxation resistance |
| Aerospace | Weight/volume control | Specific yield strength |
| Electronic strip | Resistance to permanent deformation | Stress relaxation resistance, yield strength |

strength, which provide engineered yield strengths of 95 and 110 ksi and CVNs of 30-60 and 12-20 ft-lb. Along with significant improvements (20-40%) in notch strength ratio (NSR) compared to standard hot worked (110 ksi yield strength) product at a stress intensity factor of about 3.9 and in fracture toughness, these new tempers fulfill the need for field robustness over traditional hot worked material.

*Aerospace*—Similarly in aerospace, traditional hot worked metal with 110 ksi yield strength meets performance needs in landing gear where high compression strength and resistance to galling and seizing is important. Back extrusion and other hot working methods are meeting demands for larger diameters of tubular shapes and will satisfy the need for larger, long-range jet aircraft and intermediate-range commercial aircraft for longer service of nose and main landing gear.

This effort is also creating growth in components requiring the tribological characteristics of ToughMet. In addition, the FAA-sponsored Metallic Materials Properties Development and Standardization (MMPDS) process and Aerospace Materials Specification (AMS) have established property design minimums for rod, bar, tube, and plate for the AT and TS product tempers. Extensive production and testing of these 110 and 150 ksi yield strength configurations are establishing use of ToughMet 3 in jet aircraft landing gear systems. Secondary property testing is a part of the MMPDS system, including basic tensile properties, pin bearing, compression, shear, and selected physical properties, all having a statistical basis recognized by the FAA.

Spherical bearings for aerospace use require significantly higher strength than those used in other applications due load concentration. To meet this need, a new temper with 150 ksi yield strength and increased size capability was developed to enable use in landing gear, particularly when operating with gall-sensitive titanium and PH stainless steels.

*Mechanical systems*—Ground engaging machinery, mining equipment, and internal combustion engines are finding success in adapting cast and wrought versions of ToughMet 3 for bushing and bearing applications. As such, these applications are steadily growing. The need to manage mechanical distortion during fabrication is being met by FEA methods and development of precision machining methods using designed experiments, tooling engineering, and measurement technology.

Plate and sheet forms are offered to service sliding componentry or roll formed bushings and bearings, along with rod, bar, and tube configurations in both wrought and cast forms.

*Electronics*—Copper beryllium strip has long been the material of choice for high reliability signal and power connectors and springs due to its unique combination of strength, formability, and conductivity. Although copper beryllium can be used safely, alternative materials that do not contain beryllium are desired.

A natural extension of the ToughMet 3 plate product rolled into strip form satisfies this need. BrushForm 158 is named after its nominal 15% nickel, 8% tin composition. It has strength, resilience, and formability similar to copper beryllium and can be used in spring applications where conductivity is not as important, such as in electromagnetic shielding gaskets. BrushForm 96 (based on ToughMet 2 composition) may be used for springs requiring additional conductivity.

ToughMet 3 is available in small-diameter rod and wire for machined electronic connectors, such as coaxial connectors used in telecommunications base stations and down-hole drilling equipment, as well as circular connectors used in trucks or military avionics. Its high strength, inherent resistance to both corrosion and atmospheric tarnishing, and stress relaxation resistance ensures reliable passage of critical electrical signals, similar to the performance of traditional copper beryllium alloys.

## Current trends

Demand for more mechanically robust products continues in oil and gas exploration markets and the TS tempers are beginning to satisfy this demand.

Environmental pressure is driving producers of performance components away from alloys containing beryllium, in spite of their superior attributes. In response, the Cu-15Ni-8Sn alloy and associated tempers are gaining wider use.

Strip product forms are building the basis for passive micro-mechanical products in the electronics industry.

## Future prospects

Machining of finished parts in oil and gas, aerospace, and mechanical systems necessitates a premium for the components. Additional product forms will be available to improve yields and minimize costs associated with machining, material handling, and related infrastructure.

Bearings manufactured from strip, rolled into shape, and potentially welded will reduce the cost of machining thin-walled bearings out of tube. Alternative additive manufacturing or net shape processes might be able to reduce cost and enhance overall competitiveness without sacrificing performance. New property combinations—generally higher strength with higher ductility—are a challenge that will resolve by further development, resulting in new tempers and even new alloys.

Reproducibility during the production process is a key factor in maximizing yield, throughput, and overall product consistency. Continuous improvement using lean sigma principles will increase consistency to levels in excess of $C_{pk} = 1$.

Cu-Ni-Sn spinodal alloys are poised to meet current and future demands for superior combinations of strength, tribology, corrosion resistance, toughness, formability/fabricability, optimized size and shape range, and improved reliability. ❍

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