High Modulus Reinforcement Alloys

Ke Han, Vince Toplosky, Na Min, Jun Lu, Yan Xin, and Robert Walsh

***Abstract*—Materials used as reinforcement for conductors in high-field magnets require both a high capacity for load bearing and a high resistance to deformation under stress; that is, a high value for tensile strength and a high modulus of elasticity. In addition, compatibility between the magnet conductor and any proposed reinforcement materials has to be carefully evaluated in terms of their capability for thermal expansion, stability at high temperature, resistance to oxidation, and crack propagation. We investigated a number of (nickel based and nickel–cobalt based) superalloys designed for high-temperature applications. These superalloys have higher Young's modulus than the stainless steels that are currently used as reinforcement materials for high-field magnets. Our test materials were subjected to thermo-mechanical processing that strengthens the alloys by forming very fine particles within them. Our initial work focused on changes that occured in the alloy during deformation at either cryogenic or room temperature. Because we observed distinct interfaces between the particles and the matrix, we decided that these materials could be described as precipitate-strengthened alloys. Both the strengthening component area and the matrix had more resistance to plastic deformation at cryogenic temperatures, than at room temperatures. In some cases, we further enhanced the strength of the alloy by doping them with other elements. In all the cases, these alloys permitted more efficient performance of conductors by shareing more of the load than would be possible with stainless steel reinforcement materials. This paper outlines the properties of these new alloys and establishes their compatibility with certain conductors commonly used for high-field magnets.**

***Index Terms*—High strength materials, reinforcement, failure mode, plastic deformation.**

I. Introduction

REINFORCEMENT materials are essential in most high field magnets [1]–[14]. If high field magnets are operated below room temperature, cryogenic properties of the reinforcement materials need to be assessed carefully. Researchers usually measure mechanical strength, modulus of elasticity, fracture toughness, ductility and fatigue resistance between 77 and 4 K [2]–[4], [14]. In most high field magnets, a high elastic modulus is desirable for reinforcement materials that are expected to carry as much as load possible in the coil to avoid any significant plastic strain in the conductors. Austenitic stainless steels used to be good reinforcement materials and have been used successfully for high field magnets [15]–[21]. The Young's modulus for most stainless steels, however, is below 200 GPa, lower than the value desired for very high field magnets [22]. Increasing the modulus of stainless steels without significantly modifying the chemistry is at present impossible. Because of the continuing demand for ever higher magnetic fields, researchers are now branching out into other types of high strength structural material for ever stronger magnets. Some of these reinforcement materials are made of such high modulus elements as nickel.

Manuscript received October 6, 2017; accepted January 15, 2018. Date of publication January 26, 2018; date of current version March 20, 2018. The work was undertaken in the National High Magnetic Field Laboratory, which was supported in part by the NSF under Grant DMR-1157490, in part by the State of Florida, and in part by the DOE. *(Corresponding author: Ke Han.)*

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Digital Object Identifier 10.1109/TASC.2018.2798609

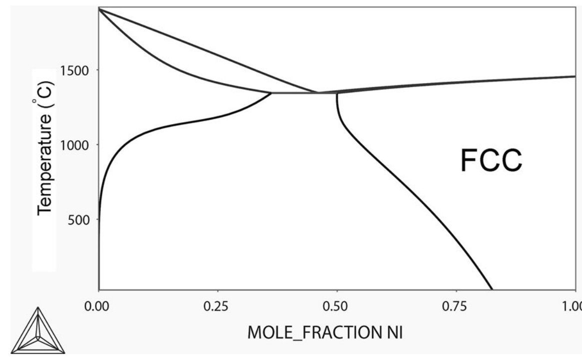

Fig. 1. Calculated phase diagram of Cr-Ni showing that Cr has a large solubility in Ni. The resulting solid solution has an fcc structure.

II. Selected Nickel Alloy Systems

Certain nickel alloy systems are reviewed in this section to discuss possibilities for the use of these alloys in new high field magnets. Phase diagrams were calculated by Thermo-Calc and used to compare different systems. Taking into account that high field magnets may operate at cryogenic temperatures, certain phase transformations resulting from cryogenic temperature are considered.

A. Nickel

Nickel has a face-centered cubic (fcc) structure, and has no defined ductile-to-brittle transition temperature. At cryogenic temperatures, pure nickel retains high elongation at fracture. In fact, pure nickel shows even higher elongation at 4 K than at room temperature because of its high strain-hardening rate.

B. Chromium Alloying Effects

Although chromium itself, unlike nickel, has a body-centered cubic structure, its solubility is up to 20 wt% in nickel (Fig. 1).

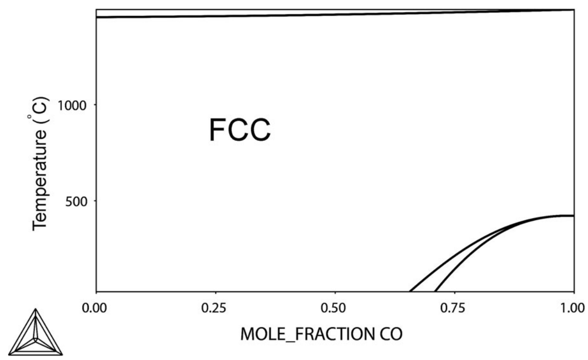

Fig. 2. Calculated phase diagram of Co-Ni showing that Co has a very large solubility in Ni. The solid solution has an fcc structure, as indicated in the figure.

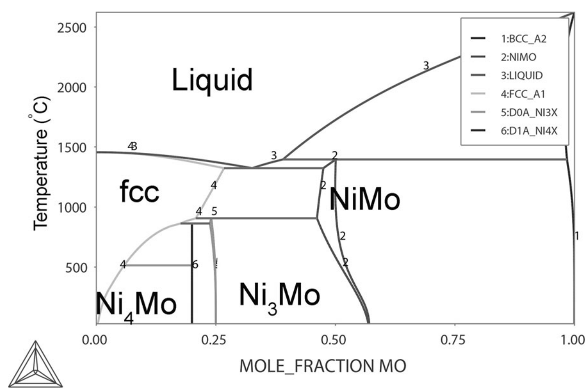

Fig. 3. Calculated phase diagram of Mo-Ni showing that although Ni solid solution can dissolve more than 10 wt% Mo, intermetallic compounds do form in this binary alloy. The solid solution has an fcc structure.

Inconel 718 is the commercial name of a reinforcement material based on nickel-chromium alloy. In most cases, this material retains an fcc structure at cryogenic temperatures. Its chromium content was designed to fall between 17 and 21 wt% but the nickel content can exceed 50 wt%.

C. Cobalt Alloying Effects

Although cobalt itself has a hexagonal crystallographic structure, it has a very large solubility in fcc nickel (Fig. 2).

Multiphase (MP) alloys were designed based on the nickel-cobalt system. These materials usually retain their fcc structure at cryogenic temperatures.

D. Molybdenum Alloying Effects

Molybdenum has a solubility slightly higher than 10 wt% in nickel (Fig. 3). Beyond this level, intermetallic compounds may form. In order to make the alloy retain its fcc structure at room temperature and below, other alloying elements, such as aluminum and chromium, are usually required.

Haynes 242 is the commercial name of a reinforcement material based on nickel-molybdenum alloys. Chromium is also added in the production of Haynes 242. We found that the matrix of this material retains its fcc structure at cryogenic temperatures.

TABLE I
YOUNG'S MODULUS OF SELECTED NICKEL ALLOYS

Temperature	Ni[a]	Inconel 718[b]	Haynes 242[c]	Elgiloy[d]	MP35N[e]	C-276f
RT[g]	210	200	221	216	226	195
77 K	224	208	237	229	238	212
4 K	>226	-	238	-	239	210

[a] Annealed Ni [24].
[b] Cryogenic measurement was done at 84 K [25].
[c] Tensile properties measured from plate.
[d] Tensile properties measured from sheet metals [3].
[e] Dynamic modulus measured from rod; extrapolated from previous work [26].
[f] Hastelloy C276 [27].
[g] Room Temperature.

E. High-Entropy Alloys

High-entropy alloys can be manufactured into single phase metals if the chemistry and the processing procedure are engineered toward cryogenic applications. Some alloys have indeed been designed to retain an fcc structure under those conditions. These alloys may potentially be useful for application at cryogenic temperatures.

III. ELASTIC MODULUS

The Young's modulus values discussed in this section were obtained from either tensile mechanical tests [14], [23] or pulse-echo and acoustic-resonance spectroscopy [3]. We used an unload/reload cycle in most cases in tensile tests after samples were subjected to plastic strain, typically 1.5 to 2.0% strain, in order to accurately measure the elastic modulus. Although Young's modulus values obtained by conventional tensile tests are slightly lower than those obtained by ultrasonic methods, this paper summarizes them together for the purpose of qualitative analysis.

A. Pure Nickel

At room temperature, the Young's modulus of pure nickel reaches 210 GPa, increases by 7% at 77 K, and rises even higher at 4 K (Table I).

B. Inconel 718

Inconel alloys were invented and tested for cryogenic temperatures and magnet applications [28]–[32]. The Young's modulus of Inconel 718, for example, is close to 200 GPa at room temperature [25]. This value is slightly higher than that of most stainless steels. At cryogenic temperatures, the modulus of Inconel 718 shows a moderate increment of 4%.

Hastelloy C-276, which is one of the most important high strength substrates for superconductors, such as Y-Ba-Cu-O [33], was designed based on nickel, chromium, molybdenum, and tungsten. Its Young's modulus values have been reported as 195 GPa at room temperature and below 212 GPa at cryogenic temperatures [27]. Although this alloy contains a large weight

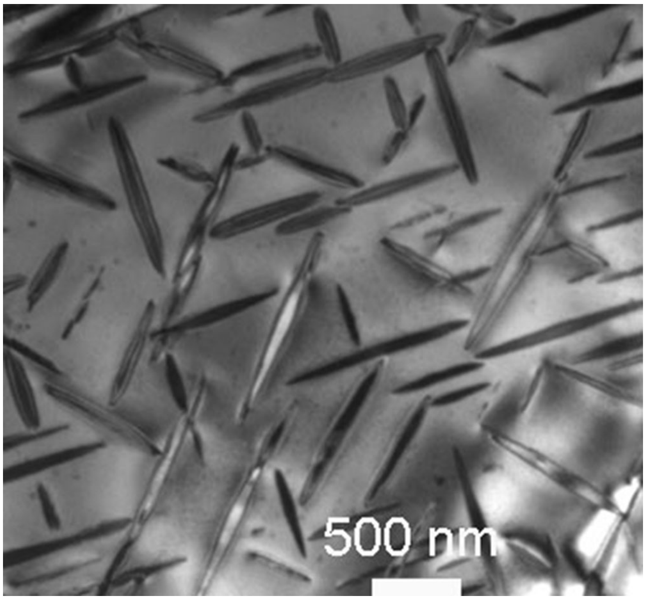

Fig. 4. Transmission electron microscopy bright field image showing the nano-sized domains of Haynes 242 aged at high temperature.

percentage of high-modulus alloying elements, the Young's modulus is not significantly higher than that of Inconel 718. Haynes International, using dynamic measurement technology, reported a slightly higher room temperature value of 205 GPa.

C. Nickel and Molybdenum

Haynes 242 is an alloy based on nickel, molybdenum and chromium. The Young's modulus of fully age-hardened alloys of this type can be as high as 221 GPa. At 77 K, the modulus is increased by 7%. The modulus is higher than those of either Inconel 718 or Hastelloy C-276 (see Table I).

In order for Haynes 242 to be considered fully aged-hardened, the materials must previously have been subjected to prolonged aging at elevated temperatures. Aging produces Ni_2Mo-type domains, which harden the alloy and enhance its elastic modulus. The size of the domains is usually smaller than 50 nm and the domains were thus called nano-sized hardening domains (NSHDs, Fig. 4). Ni_2Mo in Ni-Mo binary alloy is metastable, and is thus not included in the equilibrium phase diagram. The Ni_2Mo-type NSHDs are stabilized by the addition of Cr to the Ni-Mo alloy. The chemistry of this NSHD can be referred to as Ni_2(Cr,Mo). At relatively low temperatures, domain formation rates are relatively low. For a typical heat treatment temperature of 650 °C (the temperature at which Nb_3Sn forms in internal tin processes), full hardening requires 24 hours or longer. This range of temperature and time meets the requirement for heat treatment of Nb_3Sn-type conductors. Consequently, Haynes 242 has been chosen as one of the candidates for cable-in-conduit conductor as mentioned above.

With respect to the matrix, NSHDs form only on certain habit planes with certain specific orientations. Usually three habit planes exist in a single crystal or grain (Fig. 4). If the matrix has texture, that is, the grains are aligned in a certain crystallographic orientation, anisotropy of the elastic modulus

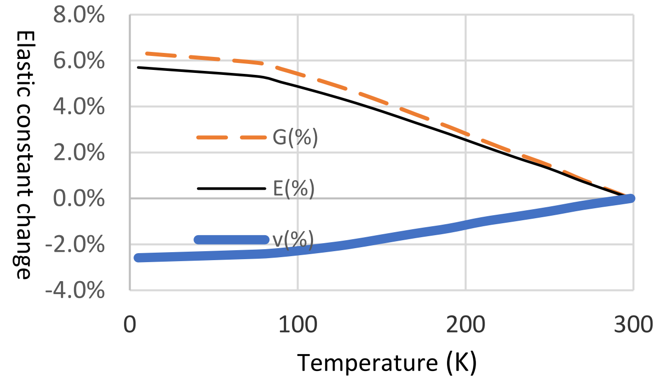

Fig. 5. Percentage change of elastic constant with temperature of MP35N alloy. The dashed line represents the shear modulus (G). The solid thin line indicates the Young's modulus (E). The thick solid line represents the Poisson ratio (v).

is likely to develop. Such anisotropy has been found in other textured nickel-based alloys, as discussed later in this paper.

One of the advantages of using Haynes 242 in wind-and-react magnets is that this alloy can be hardened after winding and it can be handled in annealed or cold-deformed condition before winding so that both the elastic modulus and the strength remain moderate, assuring easier magnet winding.

Haynes 242 is particularly compatible with Nb_3Sn-type superconducting magnets because the time and temperature requirement for the formation of the superconductor in these magnets corresponds to the requirement for hardening Haynes 242. In magnets using other types of conductor, the time required for the superconductor is significantly less than that for fully hardening Haynes 242, so the superiority of this alloy compared to less expensive stainless steel disappears. To solve this problem, certain researchers have invented a new alloy based on Ni-Mo-Cr-Re that only needs 1/36 of the age-hardening time required by Haynes 242. This new alloy also has a higher modulus than Haynes 242, which gives it additional advantage [34]–[37].

D. Nickel and Cobalt

Two nickel-cobalt alloys (MP35N and Elgiloy) have high Young's modulus and strength, and are thus very good potential candidates for cryogenic applications. Because the modulus of MP35N, which has additional alloying elements of molybdenum, is the higher of the two, we chose it as the subject of our study.

The modulus of MP35N can vary. When the alloy is fully cold-worked and age-hardened, the modulus can rise above 220 GPa, significantly higher than that of stainless steels and higher than that of alloys studied in this work (Table I). At 77 K, the modulus increases by 6%. Reducing the temperature to 5 K further increases the modulus, but at a slower rate (Fig. 5).

The shear modulus of MP35N also increases as the temperature decreases. The percentage increment of this increase is slightly higher for shear modulus than for Young's modulus (Fig. 5). This indicates that during cryogenic deformation, the alloy is more resistant to shear than to pull.

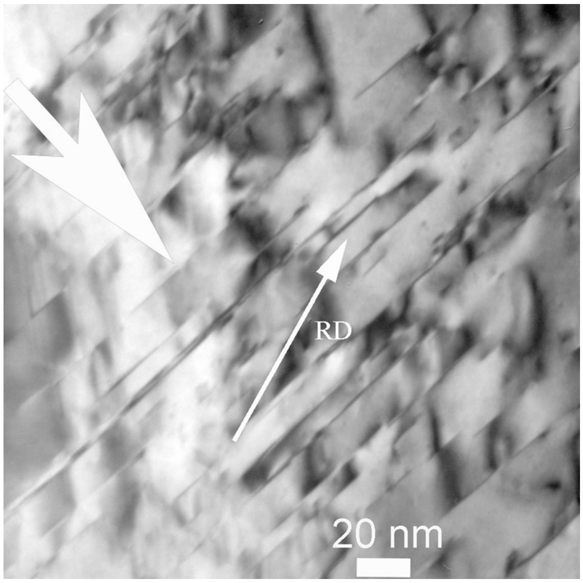

Fig. 6. Transmission electron microscopy image (bright field) showing thin platelets (one of them indicated by a fat arrow) to strengthen the materials. This sample had been cold-rolled and aged. The longer arrow indicates the rolling direction.

TABLE II
COMPARISON OF YOUNG'S MODULUS OF MP35N

Test Orientation	Temperature (K)	Young's Modulus (GPa)	Standard Deviation (GPa)
AG-LD	77	224	19
AG-TD	77	263	19
AG-LD	4	236	32
AG-TD	4	264	15

The alloy was cold-rolled to 65% and aged at 550 °C. The alloy was in sheet form. The thickness of the alloy was about 140 μm. AG indicates that the alloy was aged. LD indicates that the test direction was parallel to the rolling (the longitudinal direction) of the sheet. TD indicates that the test direction was perpendicular to the rolling (longitudinal direction) of the sheet.

Unlike most fcc alloys, MP35N has an interesting elastic constant anisotropy: the Poisson ratio (0.300) is generally smaller in this alloy than in, say, nickel (0.305-0.315), and decreases as temperature decreases, rather than remaining constant.

The strength of MP35N can be augmented by first cold-rolling and then aging, which lead to formation of layers and layers of thin platelets each only a few atoms thick (Fig. 6). After cold-rolling, the material is left with a strong texture of $<112>\{110\}$, where $<112>$ and $\{110\}$ are the crystallographic direction and plane of the texture. Similar to Haynes 242, these platelets develop a defined habit plane $\{111\}$. Textured materials usually have strongly anisotropic mechanical properties (Table II). Indeed, at both 77 K and 4 K, the values of Young's modulus in MP35N are about 10% higher in transverse direction than rolling direction.

E. High Entropy Alloys

The only data we found so far on high-entropy alloys (HEA) are from a CrMnCoFeNi fcc HEA. Young's modulus for this alloy, for example, is only about 202 GPa [24]. This value is equivalent to nickel-chromium based alloys, but lower than either nickel-cobalt or nickel-molybdenum based alloys. At 77 K, the Young's modulus of CrMnCoFeNi FCC HEA increases by 6% to 214 GPa, a percentage of temperature dependence similar to that of Haynes 242. Other than that, little is known about influence of chemistry on Young's modulus.

The shear modulus for CrMnCoFeNi HEA increases as the temperature decreases. Comparison of the shear modulus of this HEA [25] with pure Ni [25] and with MP35N [27] indicates that MP35N has a higher modulus than either of the other two alloys. The shear modulus of this HEA is about 7 GPa lower than that of MP35N, and the difference remains almost the same at all temperatures from 77 K to room temperature.

IV. OTHER MECHANICAL PROPERTIES

A. Tensile Strength

MP35N is known to have the highest mechanical strength (>2.5 GPa) of any nickel-based alloy tested at 4 K [14], [38], [39]. Since the highest level of tensile strength in MP35N has been achieved through a combination of cold-deformation and high temperature ageing, however, this alloy is suitable only for applications that require no restriction on either of these two processes.

B. Ductility and Fracture Toughness

In MP35N, the ductility tends to be low when the tensile strength is the highest [14]. If high ductility is required, the tensile strength may be compromised. As for cryogenic fracture toughness for cold-deformed and aged MP35N, no data was found when the paper was written.

Fracture toughness and ductility data are available, however, for Inconel 718 and other Inconel alloys. For higher modulus Haynes 242, fracture toughness data has only recently become available [22], [40], [41].

V. SUMMARY

Because nickel has a higher Young's modulus than iron, nickel-based alloys have the potential to produce higher modulus and higher mechanical strength than iron-based alloys for use in high field magnets. The stable fcc structure of nickel alloys also indicates that they are tough even at cryogenic temperatures. Because nickel-chromium-based alloys have a higher modulus than stainless steels, they can replace stainless steels in order to reach higher magnetic fields than ever before. In most cases, the addition of alloying elements further enhances these mechanical properties, but for reasons that are unknown, addition of a small amount of certain high modulus elements such as molybdenum and tungsten does not further significantly increase the modulus of nickel-chromium-based alloys. Even so, alloys designed around nickel and molybdenum have higher modulus than other alloys that are candidates for cryogenic magnet applications. Nickel-cobalt-molybdenum alloy has both high modulus and very high mechanical strength. Deformation and aging further enhance Young's modulus in these alloys. The aging time, however, is usually long. To shorten the required aging time, a new alloy based on Ni-Mo-Cr-Re has been introduced. Because of their modulus, strength, and cryogenic fracture toughness, these fcc-matrix Ni-based alloys are highly recommended for either reinforcement components in magnets, or as reinforced substrates for superconductors.

Acknowledgment

The authors would like to thank Drs. Ledbetter and Kim for the data of elastic constants of MP35N, Drs. Nguyen, Miller, Bird, and Mielke for their discussions of magnet design, and Drs. Tyler and Hopkins for editing the paper.

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