

Thermally stable nanostructured materials from severe plastic deformation of precipitation-treatable Ni-based alloys

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We demonstrate a means of extending the temperature range for structural applications of nanomaterials through introduction of a dispersion of precipitates, whose thermal stability determines the temperature at which strength deteriorates. Precipitate-stabilized nanostructures created via severe plastic deformation of Inconel are shown to be stable even after heat treatment for 240 h at temperatures up to one-half of the melting point. This stability results from retention of both the fine microstructure and precipitate phases at high temperatures.

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Strengthening in nanostructured materials occurs via suppression of dislocation mobility by the grain boundaries encompassing the nanometer-scale grains. However, such grain boundary strengthening inevitably entails limited ductility and inherent thermodynamic instability [1], the two main technical issues preventing widespread commercial use of high-strength nanostructured materials. Limited ductility at room temperature is as much a consequence of the fine grain sizes as the strengthening, and arises from suppression of dislocation activity. It is therefore unavoidable, and has to be taken into account during the design process. This problem has been ameliorated by developing microstructures with a bimodal distribution of grain sizes, i.e. composed of some coarse grains and other nanometer-scale grains. In such a material, some of the strength is sacrificed for enhanced material ductility [2]. In addition to improved strength, nanostructured materials also demonstrate unprecedented superplasticity at low temperatures. However, even these “low” temperatures usually entail grain growth and a concomitant loss of strength during manifestation of such superplastic properties [3].

The thermodynamic instability in nanostructured materials that leads to rapid coarsening of the micro-

structure and loss of strength is also related to the fine grain size [1]. The large surface area of the grain boundaries encompassing the nanometer-scale grains generates a large interfacial free energy and thus an increased impetus to coarsen on heating, resulting in softening. This tendency to soften in response to heating, and the resulting instability of the microstructure, remains a significant challenge for the widespread use of these remarkable materials.

Stability can be markedly improved when a dense dispersion of fine second-phase precipitates is present. However, the resulting multiphase nanostructured materials are still only as stable as the precipitates that stabilize the matrix. While solute diffusivity in the matrix is essential to the formation of precipitates, the tendency of the precipitates to coarsen in a nanostructured material is also exacerbated by the high diffusivity of the matrix [4]. We demonstrate the synthesis of a highly stable nanostructured (HSN) material of high-strength (hardness ~ 6.2 GPa) using a prototypical alloy system, Inconel 718, in which both the precipitates and the nanostructured matrix are stable even after prolonged heat treatment (~ 240 h) at temperatures as high as one-half the melting point (T_m). The design principles propounded here can be generalized to other precipitation-treatable materials and offer a new line of development for this important class of structural materials.

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The pinning force exerted by spherical precipitates of radius r and volume fraction f on a grain boundary of energy σ is $\sim \frac{f\sigma}{r}$ [5]. Therefore, the finer the precipitate size and larger their volume fraction, the greater is the grain boundary pinning and the resulting thermal stability of the microstructure. However, fine nanometer-scale precipitates may ripen rapidly with consequent loss of effectiveness in pinning the grain boundaries. Ripening of precipitates in nanostructured materials is likely to be dominated by grain boundary diffusion rather than lattice diffusion. For a precipitate of radius r , this rate of ripening $dr/dt \sim \frac{\delta D_{GB}\sigma N}{r^3}$ [6], where δD_{GB} is the grain boundary diffusivity, σ the energy of the precipitate–matrix interface and N the solute content at the grain boundary. When an alloy system with a low value of the parameter $\delta D_{GB}\sigma N$ is selected, then the precipitate ripening rate is sufficiently retarded in the temperature range of interest, thereby ensuring the overall thermal stability of the nanostructured material.

In a precipitate-strengthened nanostructured material, strengthening is due to both the precipitates (Orowan mechanism) and the fine grain sizes (Hall–Petch strengthening). The resulting material strength (τ_y) can be approximated as $\tau_y \sim \sigma_0 + kd^{-1/2} + \frac{Gb}{\lambda}$ [7], where σ_0 and k are the Hall–Petch coefficients, d is the grain size, G is the shear modulus, b is the Burgers vector and λ is the mean spacing between the precipitates. In a material such as Inconel 718, characterized by a fine precipitate spacing in the aged state, significant strengthening through concomitant grain size refinement is possible if and only if $d^{1/2}$ is comparable to λ . This necessitates typically ~ 100 nm (or smaller) grains to achieve any meaningful strengthening above and beyond what is already achievable through conventional ageing in the microcrystalline material.

Severe plastic deformation (SPD) offers a simple and viable route for achieving grain refinement down to ~ 100 nm from bulk microcrystalline materials. However, SPD of any high-strength material such as Inconel 718 by conventional methods such as equal channel angular pressing or high-pressure torsion is inherently difficult due to the tooling requirements. Here, we utilize chip formation by large-strain machining as a simple SPD route for creation of fully dense, bulk nanostructured materials of grain size ~ 100 nm, in a material system of high-strength and limited ductility [4,8,9].

Inconel 718 was solution treated by subjecting it to a temperature of 955°C for 5 h, in order to ensure that any precipitates that were initially present went into solution. The initial grain size in the solution-treated Inconel 718 was $\sim 50\ \mu\text{m}$, as measured by the Heyn line-intercept method. The solution-treated Inconel 718 was deformed to large shear strains (>4) at near-ambient temperature [9], in a single pass of the cutting tool through a suitable choice of the tool rake angle (-20°). The chip samples were in the form of bulk foils $6\ \text{mm wide} \times 0.3\ \text{mm thick} \times 100\ \text{mm long}$. The strain in the chips was estimated from measurements of the thickness change occurring during the SPD, and the rake angle, using the well-known shear plane (upper bound) model for machining [8,9].

The mechanical properties and microstructure of chips were characterized by Vickers indentation, tensile

testing and transmission electron microscopy (TEM). In the Vickers indentation, a load of 500 g was used with a dwell time of 15 s. Tensile test specimens were prepared from the chip foils with a gage length of 6 mm. These were instrumented with miniature strain gages in the gage section to measure strain. The tensile tests were performed at a strain rate of $\sim 10^{-3}\ \text{s}^{-1}$. TEM was used to characterize the grain size, dislocation substructures and precipitates.

Figure 1 illustrates the nanostructured material composed of grains typically 100 nm in size produced from the solution-treated, microcrystalline Inconel 718 due to shear strains of ~ 6 imposed using the tool. The microstructure is composed primarily of equiaxed grains, along with some elongated structures. The diffraction pattern inset in Figure 1 indicates the presence of significantly misoriented grain boundaries in this nanostructured material. Tilting experiments performed during this characterization indicated the coexistence of several low-angle dislocation structures with these highly misoriented interfaces in this severely deformed sample.

The Vickers hardness value of this microstructure was $550\ \text{kg mm}^{-2}$ ($\sim 5.4\ \text{GPa}$), nearly twice that of the undeformed bulk, microcrystalline solution-treated material ($300\ \text{kg mm}^{-2}$). Figure 2 illustrates the much-improved ultimate tensile strength of this nanostruc-

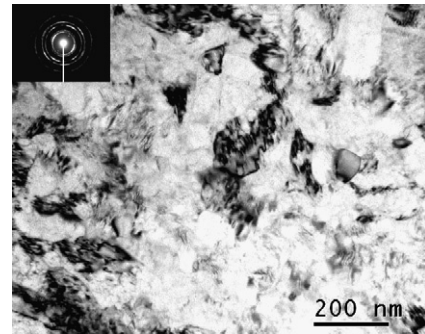


Figure 1. TEM micrograph of nanostructured Inconel 718 produced by large-strain machining (shear strain ~ 6) from solution-treated microcrystalline Inconel 718. Average grain size is ~ 100 nm. The corresponding selected-area diffraction pattern is shown as an inset.

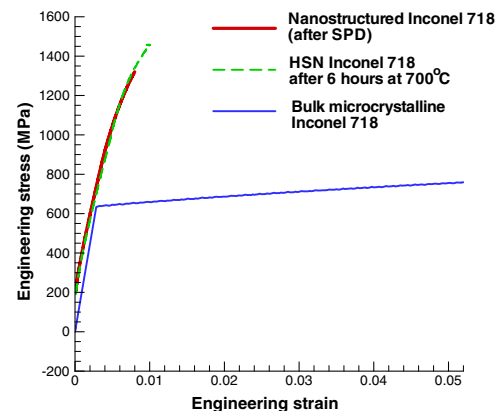


Figure 2. Stress–strain curve showing the thermal stability of the enhanced tensile strength of HSN Inconel 718.

tured material. The nanostructured Inconel is seen to possess a peak tensile strength of ~ 1.3 GPa, more than twice the yield strength of the bulk material (~ 600 MPa). As expected, its ductility is limited, but the vein-like fracture surface in Figure 3 exhibits obvious signs of micro-scale plasticity during crack propagation and fracture [10]. Interestingly, the micrometer-scale features on this fracture surface are not characteristic of fracture surfaces of typical nanocrystalline materials, which usually show submicrometer-scale dimpled features [11,12].

When this high-strength nanostructured material was heat-treated at 600°C ($\sim 0.5T_m$), a rapid hardening was realized. While we have not explicitly imaged the evolution of the ultrafine precipitates in Inconel here, such rapid hardening in nanostructured materials created from precipitation-treatable alloys is known to be due to the rapid formation of second-phase precipitates [4]. Figure 4 illustrates the variation in Vickers hardness of the nanostructured Inconel 718 at 600°C , up to 240 h of annealing. A peak hardness value of 630 kg mm^{-2} (~ 6.2 GPa) is reached after about 6 h of annealing. In contrast, precipitation of the intermetallic γ'' and γ' phases to achieve peak precipitation strengthening in the conventional microcrystalline structure usually involves a lengthier heat treatment process due to the characteristically sluggish precipitation kinetics [13]. In the nanostructured state, the large diffusion coefficient and large number of

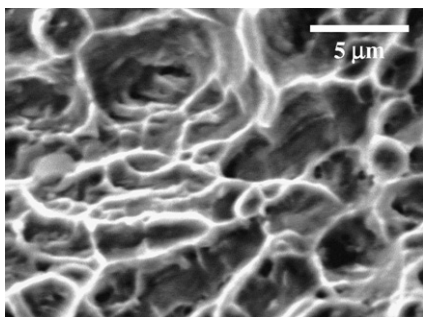


Figure 3. SEM micrograph of tensile fracture surface of HSN Inconel 718. Vein-like features are seen on the fracture surface, a manifestation of significant crack-tip microplasticity.

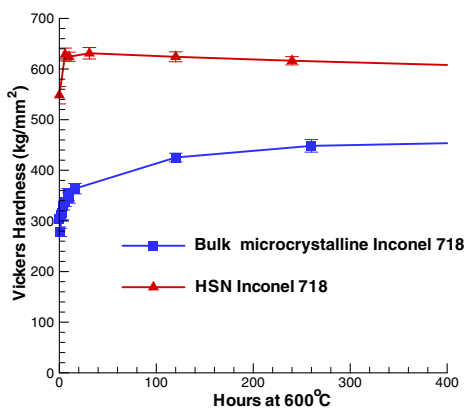


Figure 4. Variation of Vickers hardness with annealing time at 600°C for HSN Inconel 718 and bulk microcrystalline (solution-treated) Inconel 718 (grain size $\sim 50\text{ }\mu\text{m}$).

nucleation sites resulting from SPD of the solution-treated material allow for rapid precipitation of a fine dispersion. Furthermore, the Ni–Nb intermetallic γ'' phase, which can significantly contribute to material strength, is characterized by a very fine and dense dispersion of coherent, disc-shaped precipitates that are distributed in the matrix [13]. Thermal stability is also aided by the stability of the fine precipitate phase, which has been reported to have a large activation energy for coarsening of $\sim 1000\text{ kJ mol}^{-1}$ [14]. This ensures the stability of the fine precipitate phase and consequent retention of strength in the nanostructured Inconel even after prolonged annealing at 600°C , resulting in its designation as a highly-stable nanostructured (HSN) material.

Figure 4 confirms the extraordinary stability of material strength (hardness) of our HSN Inconel 718 even after prolonged annealing at 600°C . The peak hardness of 630 kg mm^{-2} is essentially unchanged throughout this heat treatment, and this hardness value is still $\sim 40\%$ greater than that of peak-aged Inconel 718 ($\sim 450\text{ kg mm}^{-2}$) in the conventional microcrystalline form. Figure 5 shows the retention of the nanocrystalline microstructure in HSN Inconel after annealing at 600°C for 10 h. This annealed microstructure is not only quite similar to that of the nanostructured material created by SPD in Figure 1, but also significantly stronger due to strengthening resulting from both the stable fine grain size and the, likely, ultrafine dispersion of precipitates. Direct characterization of these ultrafine phases in the nanostructured matrix by high-resolution electron microscopy is ongoing.

Upon annealing at 700°C ($\sim 0.6T_m$), we did not observe a strengthening as great as that at 600°C ; but the hardness value still remained stable at 5.4 GPa up to 30 h. This stable HSN Inconel after 6 h at 700°C showed a failure stress of 1.4 GPa as illustrated in Figure 2. This result also indicates an expected, albeit modest, improvement in the ductility of the HSN Inconel. This ductility is probably due to the enhanced recovery phenomena at this temperature that reduces the dislocation density while enabling precipitation from the solid solution [15]. Much more noteworthy, however, is the observation that this tensile strength following the heat treatment at 700°C is very comparable to, if not markedly greater than, that of the HSN Inconel prior to the

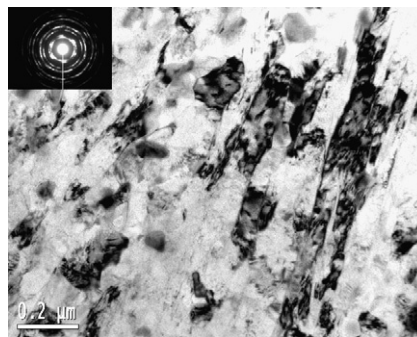


Figure 5. HSN Inconel 718 after 10 h of heat treatment at 600°C . Note similarity in grain size and negligible grain growth compared to that of the non-heat-treated nanostructured Inconel 718 of Figure 1. The corresponding selected-area diffraction pattern is shown as an inset.

heat treatment. This reinforces our observation of the extraordinary stability of the tensile strength of HSN Inconel. While prolonged annealing at 700 °C beyond 30 h was found to result in a gradual softening and loss of strength, there exists a processing window of up to 30 h at this temperature, during which HSN Inconel retains its strength, whether this is measured by the hardness or the tensile strength.

The synthesis of HSN materials by large-strain machining of precipitation-treatable alloys offers opportunities to create a new class of structural materials with significantly enhanced mechanical properties, even for difficult-to-deform alloys such as Inconel 718, PH-13 stainless steels and Waspaloy. Large-strain machining can be directly adapted to make nanostructured materials in the form of bulk foils and plates [16]; indeed, the nanocrystalline chip samples produced in the present experiments for characterization were foils. Direct production of nanostructured particulate is feasible by application of a controlled modulation to the large-strain machining process [17]. While challenges remain, consolidation of HSN particulates into bulk monolithic materials could, potentially, be accomplished with minimal loss of microstructure using processes that involve shear and elevated temperatures, or cold-spray methods. The resulting bulk HSN materials offer opportunities for advanced structural materials with interesting combinations of properties even for prolonged operation at high temperatures.

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