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Reasons for the superior mechanical properties of medium-entropy CrCoNi compared to high-entropy CrMnFeCoNi

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The tensile properties of CrCoNi, a medium-entropy alloy, have been shown to be significantly better than those of CrMnFeCoNi, a high-entropy alloy. To understand the deformation mechanisms responsible for its superiority, tensile tests were performed on CrCoNi at liquid nitrogen temperature (77 K) and room temperature (293 K) and interrupted at different strains. Microstructural analyses by transmission electron microscopy showed that, during the early stage of plasticity, deformation occurs by the glide of 1/2<110> dislocations dissociated into 1/6<112> Shockley partials on {111} planes, similar to the behavior of CrMnFeCoNi. Measurements of the partial separations yielded a stacking fault energy of 22 ± 4 mJ m^{-2}, which is ~25% lower than that of CrMnFeCoNi. With increasing strain, nanotwinning appears as an additional deformation mechanism in CrCoNi. The critical resolved shear stress for twinning in CrCoNi with 16 μm grain size is 260 ± 30 MPa, roughly independent of temperature, and comparable to that of CrMnFeCoNi having similar grain size. However, the yield strength and work hardening rate of CrCoNi are higher than those of CrMnFeCoNi. Consequently, the twinning stress is reached earlier (at lower strains) in CrCoNi. This in turn results in an extended strain range where nanotwinning can provide high, steady work hardening, leading to the superior mechanical properties (ultimate strength, ductility, and toughness) of medium-entropy CrCoNi compared to high-entropy CrMnFeCoNi.

1. Introduction

Despite what is often assumed in the high-entropy alloy (HEA) literature, and sometimes explicitly stated [e.g. Ref. [1], that configurational entropy (compositional complexity) correlates directly with the degree of solid solution strengthening, there is actually scant evidence to support this notion. In most papers where superior mechanical properties are attributed to solid solution strengthening from multiple principal elements, the results are clouded by the presence of second phases. This complicates mechanistic interpretation because of the introduction of “composite” effects. In the case of complex solid solutions with face-centered cubic (FCC) structures, Gali and George [2] first showed that increasing the number of constituent elements from four in the CrFeCoNi medium-entropy alloy (MEA), to five in the CrMnFeCoNi HEA, had negligible effect on the degree of solid solution strengthening as evidenced by their similar yield and ultimate tensile strengths. Subsequent studies [3,4] on a family of single-phase FCC alloys, including several MEAs comprising the elements present in the CrMnFeCoNi HEA, found no systematic correlation between mechanical properties and number of alloying elements (i.e., configurational entropy). For example, it was found that the ternary CrCoNi had the highest yield strength and hardness, higher than those of the quaternary and quinary alloys containing more elements. Additionally, alloys with the same configurational entropy had different strengths (e.g., FeNi was significantly stronger than FeCo, and CrCoNi was significantly stronger than MnFeNi). Interestingly, similar alloying trends were noted also for ductility, with the stronger alloys generally being the more ductile [4]. Consistent with the fact that the CrCoNi MEA [4] has higher strength and ductility than the CrMnFeCoNi HEA [2,5], it has also been demonstrated that the fracture toughness of the MEA [6] is higher than that of the HEA [7].

The microstructural aspects of plasticity in the CrMnFeCoNi HEA and its non-equiatomic counterparts have been extensively investigated during the past three years [5,8–23]. Detailed analysis of

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microstructure evolution with strain, coupled with determination of the critical stress for twinning, has greatly improved our understanding of work hardening mechanisms and reasons for the increase in strength and ductility of this HEA with decreasing temperature [16]. In contrast, despite having superior mechanical properties, the CrCoNi MEA has received little attention so far. Consequently, the microstructural origins of its high strength and ductility remain unclear. Even basic features of its plastic deformation behavior including slip planes, Burgers vectors, and dislocation dissociations, have not been reported. In addition, its stacking fault energy has not been determined. Finally, basic questions about its twinning behavior remain unanswered, including: (1) when does twinning start at 293 K and 77 K? (2) Is there a critical stress for twinning? (3) Does the twinning stress depend on temperature? (4) How does its magnitude compare to that of the CrMnFeCoNi HEA? To answer these questions and shed light on the micromechanisms of deformation and fracture in the CrCoNi MEA, we interrupted mechanical tests after several different strains and analyzed the microstructures by transmission electron microscopy (TEM). Its deformation mechanisms were then compared to those of CrMnFeCoNi to develop a better understanding of the superior mechanical properties of CrCoNi.

2. Experimental methods

2.1. Processing

An equiatomic CrCoNi alloy weighing 2.1 kg was produced by vacuum induction melting using pure elements (purity $\geq$ 99.9 wt%) as starting materials. Melting was performed in a Leybold Heraeus IS 1/III vacuum induction furnace operating at 5–20 kW. Prior to melting, the furnace chamber was evacuated to 3 mbar and then backfilled with Ar (purity, 99.998 vol%) to a pressure of 500 mbar. The raw materials were melted in a MgO crucible and poured into a zirconia-slurry coated cylindrical steel mold having a diameter of 45 mm and height of 160 mm. These processes are similar to those used for the melting and casting of the CrMnFeCoNi HEA [16,24,25]. The cast ingot was turned on a lathe to reduce its diameter from 45 mm to 40 mm, sealed in an evacuated quartz tube, and homogenized at 1473 K for 48 h. After homogenization, the quartz tube was taken out of the furnace and allowed to cool in air to room temperature, following which the alloy was removed from the quartz tube. The homogenized ingot was swaged using a four-die rotary swaging machine of type HMP R6-4-120-21S (HMP Umformtechnik GmbH, Pforzheim, Germany). In seven steps, its diameter was reduced from 40 to 16.5 mm (total true strain of ~1.8). After the final reduction, the swaged material was recrystallized for 1 h at 1173 K followed by air-cooling. Swaging was used for deformation processing of the present CrCoNi alloy since that was how we produced the CrMnFeCoNi alloy in our previous study [16]. This facilitated direct comparison of their mechanical properties.

2.2. Mechanical testing

From the recrystallized rod, rectangular dog-bone shaped tensile specimens (gauge length, 20 mm) were fabricated by electrical discharge machining such that their loading axes were parallel to the rod axis. Before the tensile tests, all faces of the specimens were ground to 1000 grit finish using SiC paper resulting in a final thickness of ~1.2 mm and a gauge section of ~4.8 mm^2. Tensile tests were performed at an engineering strain rate of 10^{-3} s^{-1} in a Zwick/Roell test rig of type Z100 at 77 K and 293 K. The room-temperature (293-K) tests were conducted in ordinary ambient air while the 77-K tests utilized a custom-built chamber filled with liquid nitrogen into which the specimens and grips were fully immersed. At 293 K, strains were measured with an extensometer attached to the gauge section and engineering stress-strain curves were obtained from these strains and the output from the load cell. At 77 K, our extensometer could not be used, so strains were determined indirectly from crosshead displacements that were corrected using the following procedure. First, 20 Vickers microindents spaced 1 mm apart were made along the gauge lengths of several tensile specimens using a force of 3.9 N. The specimens were tensile tested to different stress levels, unloaded, and the plastic strains in their gauge sections determined by averaging the change in spacing of the indents. In this way, a full engineering stress-strain curve was constructed from the different interrupted tests. This calibration curve was used to correct the crosshead displacements and obtain engineering stress-strain curves for the specimens tested at 77 K. For both test temperatures, true stress-strain curves were obtained from the engineering stress-strain curves assuming constancy of volume during plastic deformation.

2.3. Microstructural characterization

Longitudinal sections were cut from the recrystallized alloy, ground and polished with SiC abrasive papers down to a grit size of 8 μm and then with diamond suspensions down to 1 μm. Final polishing was performed with a vibratory polisher (Buehler Vibromet 2) and colloidal silica having a particle size of 0.06 μm; long polishing times up to 48 h were employed to minimize residual deformation near the surface.

Phase characterization was carried out by X-ray diffraction using a PANalytical X'Pert Pro MRD diffractometer equipped with a 4-bounce germanium (220) monochromator (Cu Kα radiation $\lambda = 0.154$ nm; 2θ range from 40° to 120°; step size $\Delta 2\theta = 0.006°$; integration time 280 s).

Chemical composition of the swaged alloy was determined at a commercial laboratory (Revierlabor GmbH, Essen, Germany), which is the same one that we had used previously [36]. Metallic elements were analyzed by X-ray fluorescence analysis (XRFA), oxygen by carrier gas hot extraction, and carbon and sulfur by the combustion IR absorption method. Additional chemical analyses were performed by us using energy dispersive X-ray spectroscopy (EDX) at an accelerating voltage of 25 kV and a working distance of 8.5 mm in a scanning electron microscope (SEM) of type Leo 1530 VP. Five locations, each covering an area of 400 μm × 300 μm and spaced 2 mm apart between the center and the outer edge of the recrystallized rod were analyzed by EDX to check whether the recrystallized alloys are chemically homogeneous.

Texture was determined by electron backscatter diffraction (EBSD) in a SEM of type Quanta FEI 650 ESEM equipped with a Hikari XP camera (EDAX, AMETEK) at an accelerating voltage of 30 kV, a working distance of 11–15 mm and step sizes between 0.3 and 1 μm. Pattern analysis was performed using the TSL OIM Analysis software (version 6.2.0). As rotary swaging is axisymmetric, the texture of the recrystallized rod is represented by an inverse pole figure (IPF) along a direction parallel to the rod axis. The IPF was calculated using the harmonic expansion method up to a series expansion degree of 22 and a Gaussian half width of 5° without imposing any sample symmetry. Texture intensities are given as multiples of a random orientation distribution (m.r.d.).

Mean grain size was determined with the Heyn linear intercept method (ASTM E112-10) using four equidistant and parallel lines of identical length per micrograph. Annealing twin boundaries were not counted as grain boundaries. Five backscatter electron micrographs, taken at locations spaced 2 mm apart between the center and the outer surface of the recrystallized rod were used for the determination of the mean grain size. Using this method, the determination of the mean grain size involved about 1000