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Microstructural stability of ultrafine-grained niobium–zirconium alloy at elevated temperatures

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ABSTRACT

The present study reports on microstructural evolution upon static annealing treatment and elevated-temperature low-cycle fatigue (LCF) of an ultrafine-grained (UFG) body-centered cubic (bcc) niobium–zirconium (NbZr) alloy, processed by equal channel angular processing (ECAP) at room temperature.

UFG NbZr showed recovery and recrystallization at homologous temperatures, which are in the same range as those of another UFG bcc material, i.e. interstitial free (IF) steel. Unlike the UFG IF steel, the UFG NbZr featured a distinct plateau of decreased hardness due to recovery at temperatures below the recrystallization limit. This was attributed to the absence of dynamic recovery during ECAP due to the low homologous temperature of $T_h = 0.11$ ($T_h = 0.16$ for IF steel) at room temperature processing.

Strain-controlled elevated-temperature LCF tests performed in vacuum revealed stable cyclic deformation response up to 600 °C ($T_h = 0.32$). At higher temperatures, but still below the static recrystallization limit (≈900 °C, $T_h = 0.43$), cyclic softening, rapid decrease of mean stress and premature failure were observed. As compared to the UFG IF steel, cyclic stability is preserved up to higher T_h due to the stabilizing effect of solid solution alloying elements, i.e. mainly Zr.

In the case of the UFG IF steel, localized grain coarsening at the crack tip caused premature failure upon elevated-temperature LCF below the static recrystallization temperature. The more stable microstructure in the UFG NbZr did not show any localized alterations in the vicinity of the crack tip, but instead slightly coarsened throughout the whole gauge length.

In combination with the results obtained on the UFG IF steel in previous studies, a comprehensive summary of the microstructural evolution of UFG bcc materials at elevated temperatures is presented.

1. Introduction

Ultrafine-grained (UFG) metals and alloys have been widely studied during the last decade, since they feature both higher strength and good ductility, as compared to their counterparts of conventional grain-size (CG). In most bulk UFG materials, this favorable combination of properties is introduced by severe plastic deformation (SPD) [1–7]. Among other SPD techniques, equal channel angular processing (ECAP) has proven suitable for creating relatively large volumes of homogenously deformed bulk UFG materials [2,3,8]. When efficient processing routes are used uniform microstructures are achieved, featuring equiaxed grains with average diameters in the sub-micron regime and a large fraction of high-angle grain boundaries (HAGBs) [9–11]. These characteristics promote nearly isotropic mechanical properties and high microstructural stability upon monotonic and cyclic loading [9,11–13].

However, a significant amount of energy is introduced into a material by SPD, causing instability of the UFG microstructure when distinct temperatures and strain amplitudes are exceeded during operation. These limits highly depend on the lattice structure and the chemical purity of the material investigated, as well as on the processing route, which determines the microstructural characteristics [9,12–15].

Above a critical temperature, recrystallization and grain growth may occur. Eventually, these mechanisms set an inherent upper limit to operating temperatures for SPD materials. Of course, they are not limited to UFG materials. However, the latter are usually more prone to grain coarsening at relatively lower temperatures since the activation energy for recrystallization is decreased by the high dislocation density present in typical SPD materials and the driving force for grain growth is high because of the high fraction of non-equilibrium grain boundaries [16]. Cyclic plastic deformation may similarly contribute to microstructural instability as additional energy is induced and strain localization may lead to

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dynamic recrystallization at temperatures significantly lower than those under static conditions [17–19].

Thermal stability of several UFG face-centered cubic (fcc) materials, especially Cu, Al and its alloys, has been studied in recent years. Also, cyclic deformation responses (CDRs) and their relation to microstructural features have been investigated for these materials [13,17,18,20,21]. However, for UFG body-centered cubic (bcc) materials, there is still a lack of knowledge regarding thermal stability and especially the effect of combined thermal and fatigue loading. In a previous study, the authors have investigated elevated-temperature fatigue behavior of UFG interstitial free (IF) steel and pointed out the microstructural mechanisms of cyclic softening at these temperatures [15]. In the present study, a comprehensive summary of microstructural evolution in UFG bcc materials at elevated temperatures under static and fatigue loading conditions is presented, combining the current results on UFG bcc NbZr and the previous results on UFG IF steel.

Two refractory niobium–zirconium (NbZr) alloys were investigated in the current study, which are both characterized by good ductility and excellent corrosion resistance in aggressive environments provided by a dense passive surface layer. Currently, NbZr alloys are often employed in nuclear power systems, but more recently, Nb-based alloys have been envisaged for biomedical applications due to their excellent biocompatibility [22–24]. The relatively low ultimate tensile strength in the CG condition is increased significantly from 250 MPa to 690 MPa by ECAP following route 16E[1] (NbZr alloy 1), without sacrificing ductility [25]. The two alloys investigated in the current study, which mainly differ in their Zr content, were chosen since the (thermal) stability of UFG fcc microstructures strongly depends on the content of alloying elements and impurities [18–20,26], and thus, the alloying content is expected to have a similar influence in UFG bcc materials as well.

Low-cycle fatigue (LCF) tests conducted in a previous study showed pronounced cyclic stability of the UFG NbZr for strain amplitudes up to 0.5% at room temperature (RT) [25]. Conventional Nb alloys are known to have favorable mechanical properties at elevated temperatures due to their high melting point. However, the stability of the UFG microstructure in NbZr at elevated temperatures has remained unexplored so far.

In order to shed light on this aspect, annealing treatments and elevated-temperature LCF tests in combination with subsequent microstructural investigations were performed.

2. Experimental procedures

The chemical compositions of the two NbZr alloys investigated are given in Table 1. Both were obtained as hot rolled plates. Billets with the dimensions of $25 \times 25 \times 175\,\text{mm}^3$ were cut from the plates by electro-discharge machining (EDM). Subsequent ECAP was performed at RT at a processing speed of 2.5 mm/s following the processing routes 16E (NbZr alloy 1) and 8E (NbZr alloy 2). The numerical characters of the routes denote the total number of processing passes while the alphanumerical characters indicate the rotation of the billets between two consecutive passes (route E processing schedule is a sequence of 180°/90°/180° rotations around the longitudinal axis). The ECAP tool used has a cross section of $25 \times 25\,\text{mm}^2$ with a sharp 90° angle die and benefits from the “sliding walls” concept [27]. For further information on ECAP, processing routes and their nomenclature, the reader is referred to [3,8].

Routes 16E and 8E have been chosen because they provide cyclically stable microstructures at room temperature with an equiaxed grain morphology and a high volume fraction of HAGBs. Moreover, using route E, relatively large volumes of homogenously deformed material can be extracted from the billets, as compared to other ECAP routes [8]. Irrespective of the higher number of passes, route 16E materials have demonstrated very similar microstructural and mechanical properties as route E with only 8 passes due to saturation effects [25,28].

All UFG NbZr specimens used in the present work were EDMed from the homogenously deformed volume of the ECAP billets and then ground in order to remove the EDM-affected surface layer. The static annealing specimens had a cuboidal shape with dimensions of $10 \times 5 \times 1.5\,\text{mm}^3$. Prior to annealing, each specimen was sealed in a silica glass tube in vacuum environment with a pressure of $p < 10^{-4}$ mbar in order to minimize oxidation processes. Heat treatments were performed, always for 1 h, at different temperatures ranging from 400 to 1200 °C in a furnace with subsequent cooling at ambient temperature. Prior to the hardness measurements, specimens were ground, starting with coarse 320 SiC paper in order to remove any potentially affected surface layer, down to a grit size of 5 μm. For the electron backscatter diffraction (EBSD) measurements, specimens were polished in an alternating process of mechanical polishing using 1 μm alumina suspension and chemical etching[2] at RT.

The dog-bone shaped specimens used for fatigue testing were also ground down to 5 μm grit size in order to provide for smooth unnotched surfaces. Fully reversed push–pull LCF tests were performed in an MTS servohydraulic testing rig equipped with a vacuum chamber. All tests were conducted in total strain control with a constant strain amplitude of 5×10^{-3} and a strain rate of $6 \times 10^{-3}\,\text{s}^{-1}$ using a high-temperature extensometer with ceramic rods and a gauge length of 12 mm. This specific strain amplitude was chosen since previous LCF studies have demonstrated cyclic stability up to that strain amplitude at RT. In addition, when taking into account the different Young’s moduli, these test parameters were supposed to yield similar plastic strain amplitudes as those obtained on IF steel in [15]. In order to avoid buckling of the relatively thin specimens, tight brackets were attached. Specimens were heated using a high frequency induction generator and a copper coil, which was adapted to the specimens’ geometry in order to provide for a homogenous temperature profile throughout the gauge section.

Temperature was controlled using a thermocouple spot-welded to the brackets. In order to obtain accurate specimen temperature levels, a calibration specimen equipped with three thermocouples in the center and at the ends of the gauge length had been used prior to fatigue testing, such that actual specimen temperature could be related to the temperature of the thermocouple at the brackets used for temperature control.

All fatigue tests were performed in vacuum at a pressure of $<10^{-5}$ mbar. Samples were heated within 60 s and tests were started directly after reaching steady state temperature in order to avoid microstructural changes prior to fatigue testing.

For subsequent EBSD microstructure analyses of the fatigued material, samples were cut from the center of the gauge section of the fatigue specimens, ground and polished the same way as described for the static annealing specimens.

TEM specimens were extracted from the same sections as those used for EBSD and mechanically ground down to 0.15 mm foil thickness. Large electron-transparent areas were obtained by ion milling with an inclination angle of ±4.5° on both sides of the specimen with 5.5 keV and 30 μA ion current. The milling affected surface layer was removed by a 1 keV and 5 μA ion beam. For the TEM investigations the microscope was operated at a nominal voltage of 200 kV.

3. Experimental results and discussion

3.1. Static annealing treatment

In Fig. 1 a comparison of hardness values after annealing treatments at different temperature levels is given for UFG NbZr and UFG IF steel. Above a critical temperature, hardness is significantly decreased – mainly due to (partial) recrystallization – in all three materials, before the final saturation hardness level is reached due to complete recrystallization. While different contents of alloying elements have shown to exert significant influence on the critical recrystallization temperature of other UFG materials due to their stabilizing effect on the microstructure [18], the critical levels in the present study are very similar for all three materials if homologous temperature is considered instead of absolute temperature values ($T_{\text{h,critical}} \approx 0.43$).

In the case of IF steel the hardness decrease at $T_\text{h} > 0.5$ is more pronounced than for the two NbZr alloys, which indicates the effectiveness of the solid solution hardening in the latter alloys. NbZr alloy 2 features higher hardness values than NbZr alloy 1 in both, UFG and recrystallized conditions. This effect could stem from either the different chemical composition or – in the UFG condition – from the processing route. In the case of the IF steel, however, different processing routes led to very similar hardness at all temperatures [15]. Hence, the differences observed in case of the NbZr

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[1] Information on ECAP and its nomenclature is given in Section 2 and in [3,8].

[2] Etchant: 25 ml ethanol, 50 ml H_2O_2, 25 ml HNO_3, 1 ml HF.