Phase-specific deformation behavior of a NiAl-Cr(Mo) lamellar composite under thermal and mechanical loads

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Abstract: Phase-specific thermal expansion behavior and mechanical deformation behavior of a directionally solidified NiAl-Cr(Mo) lamellar *in situ* composite were investigated by using real-time *in situ* neutron diffraction during compression at elevated temperatures up to 800 °C. Tensile and compressive thermal residual stresses were found to exist in the NiAl phase and Cr_{ss} (solid solution) phase, respectively. Based on the evolution of lattice spacings and phase stresses, the phase-specific deformation behavior was analyzed qualitatively and quantitatively. Estimates of phase stresses were derived by Hooke's law on the basis of a new method for the determination of stress-free lattice spacing in *in situ* composites. During compressive loading, the NiAl phase yields earlier than the Cr_{ss} phase. The Cr_{ss} phase carries much higher stress than the NiAl phase, and displays consistent strain hardening at all temperatures. The NiAl phase exhibits strain hardening at relatively low temperatures and softening at high temperatures. During unloading, the NiAl phase yields in tension whereas the Cr_{ss} phase unloads elastically. In addition, post-test microstructural observations show phase-through cracks at room temperature, micro cracks along phase interfaces at 600 °C and intact lamellae kinks at 800 °C, which is assumed as the result of increasing deformability of both phases as temperature rises.

Key words: *In situ* composites; Directional solidification; Neutron diffraction; High-temperature deformation; Thermal residual stress.

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1. Introduction

As promising candidates for high temperature structural applications in energy conversion systems[1, 2], NiAl-based eutectic composites by directional solidification were actively investigated in the early 1970s[3, 4], and have drawn renewed interest since 1990s[5-10]. The composites can provide significant enhancement in room temperature toughness and elevated temperature creep strength over monolithic NiAl. The combination of intermetallic compound NiAl and a refractory metal phase, such as Cr and Mo, is a eutectic system that has been well characterized in terms of processing microstructures and macroscopic mechanical properties. By directional solidification, *in situ* composites are derived where the NiAl matrix phase and the fibrous refractory metal phase are well aligned parallel to the growth direction of [100] for both phases[3-6, 8]. With small additions of impurity elements such as Mo and V, the fiber-matrix morphology changes to lamellar one with the two alternating phases, and the [100] growth direction to [111][3, 5, 6]. In either case, the room temperature toughness and high temperature creep strength of the composite are significantly improved compared to those of single-phase NiAl. For example, the fracture toughness of fibrous NiAl-34Cr and lamellar NiAl-28Cr-6Mo (all compositions in this paper are in atomic percent) can reach $\sim 20 \text{ MPa}\sqrt{\text{m}}$ and $\sim 24 \text{ MPa}\sqrt{\text{m}}$ at room temperature, respectively, as opposed to $\sim 6 \text{ MPa}\sqrt{\text{m}}$ for polycrystalline NiAl or the conventionally NiAl-34Cr cast alloy[5]. The creep strength of the fibrous NiAl-34Cr and lamellar NiAl-28Cr-6Mo at a strain rate of $1 \times 10^{-6} \text{ s}^{-1}$ at 1017 °C can achieve $\sim 140 \text{ MPa}$ and $\sim 160 \text{ MPa}$, respectively, compared to $\sim 20 \text{ MPa}$ for a [001] single crystal NiAl[5].

The reinforcing mechanisms are generally associated with the well-aligned microstructure and superior mechanical properties of the refractory metal phase. Heredia *et al.*[11] summarized three toughening mechanisms, namely, crack trapping, crack re-nucleation and ductile-phase bridging, for the NiAl-based fibrous/lamellar composites. Yang *et al.*[6] regarded the improved room temperature fracture toughness in a layered NiAl-Cr(Mo) composite as the result of plastic rupture of the Cr solid solution (Cr_{ss}) layers and the domain-to-domain variations in the lamellar fracture mode. In our previous study[12],

we found in a NiAl–Cr(Mo) nano-layered composite that the Cr_{ss} layers with thickness of ~400 nm can bear very high stresses and deform plastically before fracture, unlike in bulk form, where it fractures in a relatively brittle fashion at significantly lower stresses. While the above findings can help understand the mechanisms for room temperature toughness improvement, published literatures concerning the mechanisms for high temperature creep strength enhancement are sparse. Although it is expected that the refractory metal phase should play a key role in such enhancement at elevated temperatures, the knowledge of phase-specific deformation behavior are still needed to elucidate the detailed mechanisms.

The development of *in situ* X-ray/neutron diffraction techniques allow investigation of the stress-strain response of the composite and its constituent phases simultaneously[13-20]. By measuring the elastic strain in each phase, the stress partitioning between the constituent phases can be determined using Hooke's law and their contributions to the overall mechanical behavior of the bulk can be evaluated. In our prior study[12], real-time *in situ* neutron diffraction was successfully employed to estimate the phase-specific stress increments upon the applied stresses in a nano-layered NiAl–Cr(Mo) lamellar composite. Note that the thermal residual stresses are expected during directional solidification due to differences in the coefficients of thermal expansion (CTE) of constituent lamellae, which will be further discussed in this study. The total phase-specific stresses, i.e. the sum of stress increments and thermal residual stresses, were not derived, though there are two typical methods to determine the thermal residual stress. One direct method is to determine the residual elastic strain with knowledge of a reference lattice parameter of stress-free NiAl and Cr_{ss} powders. The stress-free powders are hard to obtain from the bulk composite since the powders should be nano-scale to avoid involving any nano-layers. The other indirect route is analytical solution based on total stress balance with knowledge of CTE of individual phase as well as the joining temperature at which the two phases begin to bond in solid state. The joining temperature is actually difficult to define and measure. In order to precisely examine the phase-specific deformation behavior of the composite, it requires quantitative understanding of the thermal residual stresses in individual phases in the first place.

In the present study, real-time *in situ* neutron diffraction measurements were performed during compression of a NiAl-Cr(Mo) lamellar composite to elucidate the temperature-dependent phase-specific deformation behavior, shedding light on the reinforcing mechanisms of the composite over monolithic NiAl. Post-test microstructures were also examined by a scanning electronic microscope (SEM) to acquire the temperature-dependent deformation modes.

2. Materials and experimental procedures

The NiAl-Cr(Mo) composite with the composition of 33Ni-33Al-31Cr-3Mo was produced by directional solidification in a high-temperature optical floating-zone furnace at a growth rate of $40 \text{ mm} \cdot \text{h}^{-1}$. Two other materials, monolithic NiAl with Cr solid solution [referred to as NiAl(Cr) henceforth] and a Cr solid solution alloy [referred to as Cr(NiAl, Mo) henceforth], were also produced using the same method to compare their thermal expansion behaviors in monolithic form with those of constituent phases in lamellar form, thus shedding light on the thermal residual stress state inside the composite. The compositions of NiAl(Cr) and Cr(NiAl, Mo) are 48Ni-44Al-8Cr and 78Cr-7Mo-8Ni-7Al, respectively, which are similar to those of the constituent phases (lamellae) in the composite[21]. Details of the alloy fabrication and directional solidification processes can be found elsewhere[8, 22], where similar procedures were used to produce other eutectic composites. The microstructures of the composite as examined in our prior study[12] show well-aligned lamellar morphologies both parallel and perpendicular to the growth direction (axial and transverse direction, respectively). The thicknesses of the NiAl and Cr_{ss} layers are ~800 nm and ~400 nm, respectively. Columnar grains were observed in the single-phase NiAl(Cr) and Cr(NiAl, Mo), indicating their polycrystalline morphology.

Cylindrical samples with the dimension of 6 mm in diameter and 12 mm in length were cut from the directionally solidified rods along the growth direction for *in situ* compression and heating experiments. The *in situ* compression tests were conducted on the VULCAN Engineering Materials Diffractometer at the Spallation Neutron Source, Oak Ridge National Laboratory (SNS, ORNL), as schematically illustrated in Fig.1, where the loading direction is parallel to the growth direction $\langle 111 \rangle$ of both phases in the composite. The VULCAN diffractometer was described in detail elsewhere[23], but in

brief, the loading axis is horizontal and at 45° to the incident neutron beam, allowing simultaneous measurement of lattice spacing both parallel and perpendicular to the loading direction, i.e. the longitudinal and transverse directions. Displacement control mode was used for the loading part at a rate of $2 \text{ mm}\cdot\text{h}^{-1}$, corresponding to an engineering strain rate of about $5\times 10^{-5} \text{ s}^{-1}$ (the engineering strains were calculated as the ratio of the crossheads displacement to the initial sample length), while force control mode was employed for the unloading part with a period of 30 min. These rates were chosen to ensure adequate neutron diffraction data in a quasi-continuous manner as will be discussed later. For the high-temperature tests, the sample was heated by copper induction coils at a rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$, and then held at the target temperature for 10 min before compression. During the heating and holding process, a small force of -50 N was applied on the sample to allow expanding under nearly constraint-free condition. A total of 7 samples were tested, including 6 *in situ* compression tests and an *ex situ* compression tests. The *in situ* compression tests were conducted at five different temperatures: 20, 200, 400, 600, and 800 $^\circ\text{C}$. Two *in situ* tests were conducted at 20 $^\circ\text{C}$ for the purpose of repeatability validation, one with a large stain of $\sim 3.5\%$ and the other with a small strain of 0.5%. The neutron diffraction measurements of the two tests show reasonable consistency, which will be given later. Thus only one *in situ* test was conducted at each of the other four temperatures. One *ex situ* compression was conducted at 800 $^\circ\text{C}$, in which the compressive strain achieved $\sim 10\%$ to examine the fracture mode. Axial cross-sections of the *in situ* compressed sample at 600 $^\circ\text{C}$ and the *ex situ* tested sample at 800 $^\circ\text{C}$ were examined by SEM.

Thanks to the high neutron flux available at the SNS, diffracted neutron data could be recorded continuously during the mechanical tests in real-time. This procedure is different from the conventional step-wise method of collecting neutron data, in which the mechanical loading is periodically interrupted and the sample is held at a constant load or displacement to allow enough time for the diffraction data to be collected[13, 24]. Thus, in our procedure, the creep or stress relaxation due to the holding is eliminated. When analyzing the neutron data, one can choose different time intervals to chop the data using the VDRIVE software[25]. The neutron data within the chosen time interval/bin can then be averaged, and quasi-continuous data points are obtained for the entire scan. In the present study, we found that one-

minute intervals gave diffraction patterns with sufficient statistics as shown, for example, in Fig. 2(a), where the one-minute diffraction patterns in the axial and transverse directions show almost perfect $\langle 111 \rangle$ and $\langle 110 \rangle$ orientation in the loading direction and its perpendicular direction, respectively, as schematically illustrated in the inset of Fig. 1. The NiAl phase shows a strong (111) peak in the axial direction because it has an ordered B2 structure. In contrast, the Cr_{ss} phase with the body centered cubic (bcc) structure does not exhibit the (111) peak. Meanwhile, the NiAl-(222) and Cr-(222) peaks are very close to each other due to little difference of their lattice parameters. Specially, after the bulk yielding at high temperatures, for example at 800 °C as shown in Fig. 2(b), the two (222) peaks almost merge into one peak, which makes the single peak fit analysis difficult to perform. Therefore, the NiAl-(111) peak was utilized to analyze its deformation behavior, while that of the Cr_{ss} phase was deduced according to total stress balance, as will be further discussed later.

3. Results and discussion

3.1 Thermal expansion behavior

Figure 3 (a) and (b) show the d spacing as a function of temperature in the axial and transverse direction, respectively. The values of d spacing were derived by single peak fitting over specific reflections. Due to the solid bonding of NiAl and Cr_{ss} layers, the lattice spacing of NiAl-(222) planes and Cr-(222) planes in the axial direction co-expands as temperature increases, as indicated by the parallel d spacing-Temperature curves in Fig. 3(a). In contrast as shown in Fig. 3(b), the d spacing-Temperature curves of NiAl-(110) planes and Cr-(110) planes in the composite are parallel to those in polycrystalline, respectively, indicating independent expansion of NiAl and Cr_{ss} layers in the transverse direction with increasing temperature. Note that the d spacing of NiAl-(110) planes in the composite is very close to that in polycrystalline NiAl(Cr), while the d spacing of Cr-(110) planes in the composite is relatively larger than that in polycrystalline Cr(NiAl, Mo). This can be attributed to the difference in the solid solution compositions of NiAl(Cr) and Cr(NiAl, Mo) in respect to those of NiAl and Cr_{ss} lamellae in the composite. The proximity of NiAl-(110) d spacing in the composite to that in NiAl(Cr) indicates that NiAl lamellae and NiAl(Cr) may have very similar solid solution compositions.

The d spacing as a function of temperature can be fitted by the following quadratic equation:

$$d = a + bT + cT^2 \quad (1)$$

where a , b and c are the fitting parameters as given in Table 1. Then the CTE can be determined as the ratio of the derivative of the above function to the corresponding d spacing:

$$\alpha = \frac{dd}{dT} \cdot \frac{1}{d} = \frac{b + 2cT}{a + bT + cT^2} \quad (2)$$

where α is the CTE as a function of temperature.

Figure 4 shows the calculated phase-specific CTEs of the composite in the axial and transverse direction as a function of temperature, in comparison with those of polycrystalline NiAl(Cr) and Cr(NiAl, Mo). Single-phase NiAl(Cr) exhibits larger CTE than single-phase Cr(NiAl, Mo). The transverse CTEs of NiAl and Cr_{ss} layers in the composite are found very close to those of single-phase NiAl(Cr) and Cr(NiAl, Mo), respectively, indicating free expansion of individual phase in the transverse direction. In contrast, the axial CTEs of NiAl and Cr_{ss} layers in the composite are close to each other but smaller and larger than those of single-phase NiAl(Cr) and Cr(NiAl, Mo), respectively, due to the co-expansion of bonded layers. However, the axial CTE of NiAl layers becomes relatively larger than that of Cr_{ss} layers as temperature increases, e.g. $1.502 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ for NiAl and $1.466 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ for Cr_{ss} at 800 $^\circ\text{C}$, which means that the NiAl phase begins to expand more than the Cr_{ss} phase at certain high temperature. A similar behavior is observed in a NiAl-Mo eutectic composite, where the Mo_{ss} fibers expands more than the NiAl matrix in the axial direction between 650 and 800 $^\circ\text{C}$ [26]. This behavior appears to be associated with the creep of the NiAl phase as the temperature increases. The NiAl compound has been reported to possess poor creep resistance at elevated temperatures[1, 5, 27]. With the accommodation of creep, the NiAl phase expands more readily at higher temperatures.

3.2 Mechanical deformation behavior

The macroscopic stress-strain curves under compressive loading-unloading conditions at different temperatures are shown in Fig. 5. The yielding strength of the composite is significantly reduced as temperature increases, except for the case at 400 $^\circ\text{C}$ where the yielding strength is almost as high as that at

200 °C. The plastic strain hardening rate, i.e. the slope of the stress-strain curve after the bulk yielding, tends to decrease as temperature rises.

Figure 6(a) and (b) show the microstructure in the axial cross-section of the *in situ* compressed sample after a strain of ~9.5% at 600 °C. The dark and light phases are the NiAl phase and Cr_{ss} phase, respectively, with a width ratio of 2:1. Although no macro cracks were observed on the outer surface of the sample, micro cracks were found evident inside the sample along some of the phase interfaces, as shown by the arrows in Fig. 6(a). Some micro cracks seem to be arrested by the Cr_{ss} layer as shown by the circled area in Fig. 6(b). These phenomena are similar to what we observed in the compressed samples at room temperature in our previous study[12], where phase-through cracks formed but were arrested by Cr_{ss} layers. Whereas at 800 °C, after a compressive strain of ~10%, the sample showed no micro cracks but intact lamellae kinks in the axial cross-section, as shown in Fig. 6(c) and (d). In fact, the kinks as a result of the consistent bending or buckling of the NiAl and Cr_{ss} lamellae might prohibit the crack initiation by redistributing the loads, as schematically illustrated in Fig. 6(d). A small part of axial load σ is transferred to the direction normal to the interface, $\sigma_{\perp}$, which does not contribute to the delamination as the shear component along the interface, $\sigma_{\parallel}$, does. Collectively, the composite becomes more resistant to crack initiation or lamellae delamination at 800 °C than at the temperature of 600 °C and below. A possible mechanism for such phenomenon is that the NiAl and Cr_{ss} lamellae become more malleable as temperature increases and can deform more coherently.

3.3 Phase-specific deformation behavior

To elucidate the mechanisms of these macroscopic deformation behaviors, the knowledge of phase-specific deformation behavior is required, which can be inferred from the evolution of lattice spacing in individual phases as discussed below. In general, variations of lattice spacing reflect the elastic component of overall deformation, and constant lattice spacing during loading indicates occurrence of plastic deformation.

3.3.1 Qualitative understanding

As aforementioned [Fig. 2(b)], the NiAl-(222) and Cr-(222) peaks merge together after bulk yielding at high temperatures, so it is difficult to distinguish the lattice spacings of (222) planes of NiAl and Cr_{ss} phases. But the stand-alone NiAl-(111) reflection can still provide the lattice spacing of NiAl phase, and then the deformation behavior of Cr_{ss} phase can be deduced from those of the bulk composite and NiAl phase. Figure 7 shows the response of NiAl-(111) lattice spacing to the applied stress at different temperatures during the loading-unloading process. Three distinct stages are observed during loading and two during unloading, as marked by Roman number from I to V. Stage III appears to be a temperature dependent stage, showing the opposite changing trend of lattice spacing at 20-200 °C and 400-800 °C. Thus two deformation modes are generalized in Fig. 9 with schematic illustration of lattice deformation.

We first discuss the phase-specific deformation behavior during loading. In stage I, the lattice spacing decreases with the increase of compressive stress in a linear fashion, indicating that the NiAl lattice elastically responds to the applied load. When the applied stress is high enough, the critical resolved shear stress (CRSS) is reached, slipping occurs in the NiAl lattice matrix, and NiAl phase starts to yield. This theory explains the constant lattice spacing in stage II. The <111> orientation is known as the ‘soft’ orientation in NiAl because of the low critical resolved shear stress in this direction[27]. In a polycrystalline NiAl, the grain families with <111> orientation parallel to the loading direction are also reported to yield at low stress while other grain families bear the further increased load until their yielding[28]. In the present lamellar composite, since the NiAl phase cannot carry more loads after its yielding, the further increment of applied loads could only be carried by the Cr_{ss} phase. Thus the Cr_{ss} phase plays the similar role as the other grain families in the polycrystalline NiAl.

When entering stage III, the bulk composite yields along with that of Cr_{ss} phase, and the NiAl phase begins to exhibit different deformation behaviors at different temperatures. At relatively low temperatures (20 and 200 °C), the NiAl-(111) lattice spacing is further decreased, indicating that NiAl phase starts to carry additional loads after the bulk yielding, which is not observed for the <111> grain families in the polycrystalline[28]. Such reinforcement in the NiAl phase probably benefits from the well-

aligned lamellar structure. Dislocations in the NiAl layers may be arrested at the interface of the two phases, which forces the NiAl phase to yield more dislocations to accommodate the bulk deformation. This would enhance the dislocation density, thus leading to the increase of yielding stress, i.e. the so-called 'strain hardening'. At relatively high temperatures (400, 600 and 800 °C), although the applied load is increasing, the NiAl-(111) lattice spacing is slightly recovered, indicating that NiAl phase starts to carry fewer loads, i.e. it softens. Enhanced dislocation annihilation could be one possible reason for the softening of NiAl phase at elevated temperatures. In fact, dislocation density is known to be proportional to peak width, conventionally noted by full width at half maximum (FWHM)[19]. Figure 8 shows significant increase of FWHM at 20 °C but slight increase at 600 °C, which indicates rising dislocation density with plastic strain at 20 °C but almost constant dislocation density at 600 °C. Creep deformation may also help NiAl phase 'relax' by accommodating the overall deformation of the composite, considering the poor creep resistance of NiAl at elevated temperatures[1, 5, 27]. In the meantime, the bulk composite still displays strain hardening, which hence should be attributed to the hardening of the Cr_{ss} phase. The high-stress bearing capacity of the Cr_{ss} phase at all temperatures may also benefit from the nano-layered structure. The Cr_{ss} nano-lamellae may have very low initial dislocation density, in which case very high strengths can be achieved, similar to what has been reported for Mo_{ss} fibers in a directionally solidified NiAl-Mo composite[29-31].

During unloading, the NiAl-(111) lattice spacing first increases linearly with the decrease of applied stress in stage IV, and then keeps constant till unloading to zero in stage V. These behaviors seem as the mirroring acts of those in stage I and II. Thus we may explain the deformation behavior of NiAl phase in stage IV and V as that NiAl phase first elastically responds to the applied loads in compression and tension successively, and then yields in tension. A similar behavior is observed in nanoscale aluminum films with the thickness of 200-400 nm, subjected to uniaxial tension, that reverse yielding occurs during unloading, even at large overall tensile stresses[32]. The possible mechanism for the reverse yielding of NiAl phase during unloading could be related to the constraint of Cr_{ss} phase. Due to the higher CRSS, the lattice spacing in the Cr_{ss} phase has a larger elastic activity range than in the NiAl

phase. Thus the elastic recovery of Cr_{ss} phase during unloading requires accommodating deformation in NiAl phase that may be larger than the elastic activity range of its lattice spacing. Consequently, the NiAl phase yields plastic deformation in tension during unloading from large overall compressive stresses.

3.3.2 Quantitative understanding

During solidification of the lamellar composite from the solidification temperature, the different CTEs of individual layers result in the difference in thermal deformation, which can be accommodated by creep when the temperature is high enough. Below a certain temperature as called the joining temperature, the layers become bonded and internal stresses start to develop[33].

For the lamellar composite in this study, considering the well-aligned microstructure with both phases <111> oriented in the loading direction, internal stresses are estimated by the application of Hooke's law as in a uniaxially loaded single crystal case[13]:

$$\sigma^{Phase} = E_{<111>}^{Phase} \times \varepsilon_{<111>}^{Phase} \quad (3)$$

where σ^{Phase} is the phase-specific stress, $E_{<111>}^{Phase}$ and $\varepsilon_{<111>}^{Phase}$ are the phase-specific elastic modulus and lattice strain for the <111> orientation. Note that the real phase-specific stress state in the lamellar composite is as a matter of fact multiaxial and non-uniform due to the constraints of phase interface in the axial direction and in the direction that is perpendicular to both axial and transverse direction. However, the above simplified equation can still be employed to estimate the average phase stress by using the diffraction elastic modulus. The diffraction elastic modulus is defined as the slope of *applied stress-lattice strain* curve in the initial linear stage[13], which can be viewed as an equivalent elastic modulus under multiaxial stress state to that under uniaxial stress state. Lattice strain is defined by using the well-known engineering strain concept:

$$\varepsilon^{hkl} = \frac{d^{hkl} - d_0^{hkl}}{d_0^{hkl}} \quad (4)$$

where ε^{hkl} and d^{hkl} are the lattice strain and lattice spacing of specific *hkl* reflection, respectively; d_0^{hkl} represents the reference lattice spacing under stress-free condition.

As long as below the joining temperature, the NiAl phase is expected to have a tensile residual stress due to its larger CTE, and the Cr_{ss} phase a compressive residual stress. Although there is a typical analytical solution for thermal residual stresses in the lamellar structure[33], the key parameter, joining temperature, is difficult to determine. Another typical method is using diffraction techniques to directly derive the residual strain based on a stress-free powder reference[13, 34, 35]. However, for the present nano-layered composite, the difficulty in obtaining the stress-free powder is to make powders containing no bonded NiAl-Cr_{ss} layers. It is also a bold choice to select the single-phase NiAl(Cr) and Cr(NiAl, Mo) as the references, because they may not have exactly the same composition as in the lamellae of the composite, which would result in unexpected deviation from the real value.

As a matter of fact, we can use an indirect route to obtain the stress-free lattice parameter for the NiAl phase through the loading-unloading procedure of the bulk composite, as illustrated in Fig. 7 and Fig. 9. Before loading, the NiAl phase is under tensile residual stress, thus with the NiAl-(111) plane spacing $d_I = d_0 + \Delta d_r$, where Δd_r is the spacing change induced by tensile residual stress. In stage I, the NiAl-(111) plane spacing is compressed with the applied loads until a limit d_{cc} is reached, where d_{cc} is the critical compression lattice spacing at the CRSS. By defining the compressive change from the stress-free spacing to the critical spacing as Δd_{cc} , we can attain $d_{II} = d_0 - \Delta d_{cc}$. With further loading in stage II, the plane lattice spacing does not change any more, and plane slipping occurs to accommodate the overall compressive deformation. When entering stage III, the lattice spacing is further compressed at relatively low temperatures but released a bit at high temperatures. During unloading in stage IV, the lattice spacing is released gradually to the stress-free state and then further tensioned to the critical tension limit d_{ct} , which is the critical tensile lattice spacing at the CRSS. With a similar definition in stage II, we can attain $d_V = d_0 + \Delta d_{ct}$. In stage V, the plane spacing keeps constant as in stage II, and tensile plastic deformation takes place in NiAl phase though the bulk sample exhibits compressive residual strain. Assuming that the change from the stress-free spacing to the critical spacing is equal in tension and compression, i.e. $\Delta d_{ct} = \Delta d_{cc}$, then the stress-free spacing can be derived as $d_0 = (d_{II} + d_V)/2$. In

other words, the range between the saturated d spacing in stage II and V could represent the elastic activity range including both tension and compression. If no hardening is introduced, the middle point of this range can be regarded as the zero-stress state, as marked “ d_0 ” in Fig. 7. Such conjecture is actually proved valid at high temperatures in Fig. 7(d) where the saturated d spacing in stage V remains almost the same after unloading from different plastic strains [Fig. 5]. In the room-temperature case, it seems that the saturated d spacing is not fully achieved in stage V of the test having much plastic strain [with solid circle symbols], which may be associated with the strain hardening in stage III. Another *in situ* compression test was done at room temperature with less plastic strain, showing distinctly a saturated d spacing in stage V [with hollow circle symbols]. Also note that the data of the two tests at room temperature show a good agreement in stage I and IV, confirming the repeatability of the neutron diffraction measurements. Thus, a reasonable stress-free lattice spacing d_0 of NiAl phase can be determined for each temperature.

Note that the above method to determine the d_0 of two-phase materials is based on two assumptions. (a) The critical shear stress during tensile and compressive loading does not differ significantly, when neither twinning nor phase transformation is the main deformation mode. (b) The stress partitioning ratio must remain constant during the elastic loading stage. In our case, no twinning or phase transformation is observed during deformation, and the lattice spacing of the two phases is compressed linearly with applied loading before yielding. Therefore, the two assumptions might stand in the studied nano-lamellar composites.

Before moving on to the calculation of thermal residual stresses, the experimentally determined stress-free lattice spacings d_0 are compared with NiAl-(111) d spacings in solid solution alloy NiAl(Cr) as a function of temperature, as presented in Fig. 10. The values of stress-free spacing d_0 seem to fall on the path of NiAl-(111) d spacings in NiAl(Cr). Recall that NiAl-(110) d spacing in the composite is very close to that in NiAl(Cr) [Fig. 3(b)], which indicates that in the present study the solid solution alloy NiAl(Cr) may serve as the stress-free reference for the NiAl phase in the composite. The above results in Fig. 10 may in turn reflect the validity of the experimentally determined stress-free lattice spacing d_0 .

With the stress-free lattice parameters determined above, the thermal residual stresses in the NiAl phase can be obtained by Hooke's law at temperature T :

$$\sigma_r^{NiAl}(T) = E^{NiAl}(T) \varepsilon_r^{NiAl}(T) = E^{NiAl(111)}(T) \cdot \frac{d^{NiAl(111)}(T) - d_0^{NiAl(111)}(T)}{d_0^{NiAl(111)}(T)} \quad (5)$$

where the subscript ' r ' stands for '*residual*', and $E^{NiAl(111)}$ is the diffraction elastic modulus as given in Table 2.

In the lamellar structure with infinite layers, the total stress balance must be met:

$$\sigma_r^{NiAl}(T) t^{NiAl} + \sigma_r^{Cr}(T) t^{Cr} = 0 \quad (6)$$

where t is the thickness of individual layer. Thus the residual stress in the Cr layers is derived as:

$$\sigma_r^{Cr}(T) = -\sigma_r^{NiAl}(T) \cdot \frac{t^{NiAl}}{t^{Cr}} \quad (7)$$

The calculated phase-specific thermal residual stresses are given in Fig. 11. The NiAl and Cr_{ss} phases are seen to have a tensile and compressive residual stress, which reaches as high as ~-190 MPa and ~-380 MPa at room temperature, respectively. As the temperature goes beyond 200 °C, the thermal residual stresses are found to drop significantly, and nearly diminish at 800 °C, which is expectable considering that the mismatch of thermal expansion deformation between the two phases becomes less at higher temperature. The softening of the NiAl phase observed in Fig. 7 may also contribute to the relief of residual stresses at elevated temperatures, since an isothermal holding of 10 min was conducted before compression loading.

Similarly, the phase-specific stresses during compression loading can also be derived by following the above procedure taking the applied stress into consideration:

$$\sigma_r^{NiAl}(T) t^{NiAl} + \sigma_r^{Cr}(T) t^{Cr} = \sigma_{applied} \quad (8)$$

where $\sigma_{applied}$ is the applied stress on the bulk. Thus the stress in the Cr layers is derived as:

$$\sigma_r^{Cr}(T) = \sigma_{applied} - \sigma_r^{NiAl}(T) \cdot \frac{t^{NiAl}}{t^{Cr}} \quad (9)$$

The calculated phase-specific stresses are shown in Fig. 12. Apparently, during compression loading, the applied load adds to the compressive residual stress in Cr_{ss} phase [Fig. 12(b)], but it has to first overcome the tensile residual stress in NiAl phase before undergoing compression [Fig. 12(a)]. In other words, the NiAl phase is reinforced by the tensile residual stress to carry more load under compression, however, its loading capacity (defined as the stress increments from the start of loading till its yielding for individual phase) is still far lower than that of the Cr_{ss} phase, for example, ~500 MPa and ~1700MPa for NiAl and Cr_{ss} phase at room temperature, respectively. After the obvious bulk yielding, i.e. the yielding of Cr_{ss} phase, the Cr_{ss} phase shows consistent strain hardening at all temperatures, whereas the NiAl phase exhibits remarkable strain hardening at relatively low temperatures (20-200 °C) but tends to soften at high temperatures (400-800 °C) as manifested by the decrease of phase stress with the increasing applied strain. Hence the decrease of plastic strain hardening rate with increasing temperature seen from Fig.5 is mainly due to the softening of NiAl phase. It is worth noting that the phase stress level of Cr_{ss} phase after yielding is even higher at 400 °C than at 200 °C, which explains the close levels of yield strength at 200 and 400 °C. This behavior is presumably attributed to the dynamic strain aging in the solid solution Cr_{ss} phase. Dynamic strain aging, as generally referred to as the interaction between mobile dislocations and solute atoms in certain temperature range[36, 37], has been reported to cause abnormal hardening of solid solution alloys[38-40].

During unloading, the Cr_{ss} phase shows an elastic unloading behavior, while the NiAl phase starts to yield at the end of unloading. This confirms our prior assumption that the elastic recovery of Cr_{ss} phase during unloading causes accommodating deformation in NiAl phase larger than its elastic activity range. After unloading, tensile and compressive residual stresses exist in NiAl phase and Cr_{ss} phase respectively, which are larger than their initial thermal residual stresses before loading. This fact indicates that the mismatch of mechanical deformation between the two phases during the loading-unloading process is more than that of thermal deformation during cooling down from solidification temperature.

4. Conclusions

The temperature-dependent phase-specific deformation behavior of a directionally solidified NiAl-Cr(Mo) lamellar composite was investigated by post-test microstructural observations and real-time *in situ* neutron diffraction during compression. The CTEs of constituent phases in the axial and transverse directions were derived. Phase-specific deformation behavior under mechanical loads were discussed both qualitatively and quantitatively in terms of evolution of lattice spacings and phase stresses, respectively. The phase stresses were estimated by Hooke's law on the basis of a new method for the determination of stress-free lattice spacing in *in-situ* composites. Important results and conclusions are stated as follows:

- (1) The deformation mode changes from phase-through cracks at room temperature, to micro cracks along phase interfaces at 600 °C, and to intact lamellae kinks at 800 °C. This transition is assumed to benefit from the enhanced deformability of both NiAl phase and Cr_{ss} phase as temperature rises.
- (2) In the axial direction, tensile and compressive thermal residual stresses exist in the NiAl phase and Cr_{ss} phase below the joining temperature, respectively, due to the mismatch of their CTEs.
- (3) During compressive loading, NiAl phase yields earlier than the bulk composite, and the bulk yielding is caused by that of Cr_{ss} phase. During unloading, NiAl phase yields in tension while Cr_{ss} phase unloads elastically.
- (4) The Cr_{ss} phase undergoes much higher stress than the NiAl phase, and exhibits consistent strain hardening at all temperatures, whereas the NiAl phase displays strain hardening at relatively low temperatures (20-200 °C) and softening at high temperatures (400-800 °C).

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Fig.1 Schematic of *in situ* neutron diffraction during compression of the NiAl-Cr(Mo) composite.

Fig.2 One-minute diffraction patterns of the composite in the test at 800 °C. (a) Axial and transverse diffraction patterns at room temperature; (b) Evolution of NiAl-(222) and Cr-(222) reflections during heating from room temperature to 800 °C, and then iso-thermal holding, loading, and unloading.

(a)

(b)

Fig.3 The d spacing as a function of temperature in the (a) axial direction and (b) transverse direction.

Fig. 4 Phase-specific CTEs of the composite in the axial direction [NiAl-(222), Cr-(222)] and transverse direction [NiAl-(110), Cr-(110)], compared to those of polycrystalline NiAl(Cr) and Cr(NiAl, Mo).

Fig.5 Stress-strain curves of the composite at different temperatures: (a) the whole loading-unloading process and (b) initial loading part. The gaps at 20 °C and 600 °C correspond to the absence of neutron data. An intermediate unloading-reloading was done at 600 °C.

Fig. 6 Post-compression microstructures of NiAl-Cr(Mo) composite samples after compressive strains of ~10% at (a)-(b) 600 °C and (c)-(d) 800 °C.

Fig.7 Determination of stress-free reference d_0 from evolution of d spacing of NiAl-(111) planes during loading and unloading at different temperatures: (a) 20 °C, (b) 200 °C, (c) 400 °C, (d) 600 °C and (e) 800 °C. For the sake of clarity, error bars associated with the neutron measurements are only shown in the room temperature case in (a). The results of a second *in situ* compression test with less plastic strain [almost no stage III] were shown as yellow hollow circles for comparison.

Fig. 8 Evolution of FWHM during compression loading at 20 °C and 600 °C

Fig. 9 Schematic illustration of evolution of the NiAl-(111) plane spacing during a loading-unloading cycle. The two inner left and right graphs represent the applied stress vs. d spacing relations at relatively low temperatures (20-200 °C) and high temperatures (400-800 °C), respectively. The red solid lines and blue solid lines indicate the loading and unloading sections, respectively. The six outer sets show the states of NiAl-(111) lattice planes at the six corresponding points noted as black dots on the inner graphs. The red dash lines stand for the slip planes.

Fig. 10 Comparison of stress-free d_0 of NiAl-(111) lattice planes determined experimentally to the NiAl-(111) d spacings in the composite and NiAl(Cr) solid solution..

Fig.11 Phase-specific thermal residual stresses in the axial direction as a function of temperature.

Fig.12 Calculated phase stresses in (a) NiAl phase and (b) Cr_{ss} phase during compression at different temperatures.

Table1 Fitting parameters of d spacing with temperature for different reflections

Para- meter	NiAl(Cr) NiAl (110)	Cr(NiAl,Mo) Cr (110)	Composite NiAl (111)	Composite NiAl (222)	Composite Cr (222)	Composite NiAl (110)	Composite Cr (110)
a	2.036023	2.054266	1.666769	0.833538	0.839837	2.035225	2.057048
b	2.73E-05	1.76E-05	1.97E-05	9.88E-06	9.98E-06	2.72E-05	1.72E-05
c	4.14E-09	5.02E-09	3.50E-09	1.73E-09	1.54E-09	4.16E-09	6.02E-09

Table2 Diffraction elastic modulus of NiAl phase in the axial direction

NiAl (111)	Temperature (°C)				
	20	200	400	600	800
Diffraction elastic modulus (GPa)	260	247	229	218	210