Comparative Analysis of Nanostructure and Phase composition of Amorphous and Polycrystalline Al\textsubscript{85}Ni\textsubscript{7}Fe\textsubscript{4}La\textsubscript{4} Alloys after Complex Impacts of Deformation and Flash Lamp Annealing

N D Bakhteeva, E V Todorova

Institution of Russian Academy of Sciences A.A. Baikov Institute of Metallurgy and Material Science RAS, Russia, Moscow, Leninsky av., 49

E-mail: otnatalia@yandex.ru

Abstract. The structure and phase composition of an aluminum-based alloy Al-Ni-Fe-La with two types of initial structure (polycrystalline and amorphous) after complex action of plastic deformation and pulsed photonic processing were studied by metallography, X-ray diffraction analysis, and differential scanning calorimetry. It was found that in alloys of both types, after intensive plastic deformation (IPD), a multiphase nanostructural state is formed. In a polycrystalline alloy, IPD develops the dispersion of all phase components present in the alloy after quenching. In an amorphous alloy, IPD causes the development of partial multiphase crystallization, which is not completed in the entire range of the studied deformation parameters. The retained amorphous phase and high dispersion of all phase components in the amorphous alloy provide increased values of hardness in comparison with the hardness of a polycrystalline alloy under all investigated deformation modes. It is shown that preliminary deformation increases the stability of the amorphous alloy to temperature. Complex processing, including IPD and FLA, leads to additional hardening of alloys. The optimal mode of complex action on the structure, which ensures their maximum strength characteristics, has been determined. The hardness of the alloy with the initial amorphous structure remains higher in the entire investigated range of complex processing parameters.

1. Introduction

Among the promising materials of the new generation, quick-hardening aluminum alloys doped with rare-earth and transition metals attract attention. Depending on the composite alloying and cooling parameters from the melt, it is possible to form structures of various morphological types in such alloys: amorphous or polycrystalline. The use of new processing technologies-intensive plastic deformation (IPD), flash lamp annealing (FLA) and laser processing - allows us to create nanocrystalline composite structures in such alloys that have increased strength and plastic mechanical characteristics.

The purpose of this work was to optimize the modes of complex processing of an aluminum-based alloy with an increased content of transition and rare earth metals Al\textsubscript{85}Ni\textsubscript{7}Fe\textsubscript{4}La\textsubscript{4}, including quenching at different speeds from the liquid state, IPD and FLA, in order to create a multiphase nanocomposite structure with an increased set of mechanical properties.
2. Experimental

A comparative analysis of the structure, phase composition and some mechanical properties of the \text{Al}_{85}\text{Ni}_{7}\text{Fe}_{4}\text{La}_{4} alloy after various types of cooling (in air and under spinning conditions), as well as after complex processing, including an 8 GPa shear IPD with a twist angle of the movable anvil $\varphi=360^\circ\times1...360^\circ\times6$ (Bridgman method) and pulsed photon processing (FLA) using xenon lamps with a fluence of $F=10...25$ J/cm$^2$, was carried out on the basis of the results obtained by X-ray diffraction (XRD), metallography (Axiovert 40MAT optical microscope) and differential calorimetry. The phase composition of the alloy was studied by XRD on a DRON-3M diffractometer using Cu Ka-radiation. Phase analysis of the X-ray diffraction patterns was performed using PDF-2 data. The phase-transition temperatures were determined at a constant heating rate ($20^\circ$/min) on a SETARAM DSC 111 calorimeter. The microhardness of the samples was measured on a 402 MVD – Wolpert Wilson Instruments microhardometer at a load of 10 g and a loading time of 10 sec.

3. Result and discussion

Figure 1 shows diffraction patterns of samples after cooling at two speeds. The presence of multiple intensity peaks on the diffraction pattern "a" indicates the formation of a polycrystalline multiphase structure in an ingot crystallized in air. Complex analysis of the microstructure by XRD and metallography methods showed that the dendritic structure of the alloy contains a solid solution of aluminum and intermetallic phases \text{Al}_{9}\text{Ni}_{2-x}, \text{Al}_{11}\text{La}_{3}, \text{Al}_{8}\text{Fe}_{2-x}\text{Ni}_{x}\text{La}. The high content of iron and nickel in the alloy does not exclude the presence of intermetallics Al$_{13}$Fe$_4$ (monoclinic lattice) and Al$_{8}$Ni$_{1-x}$Fe$_x$ (rhombic lattice). These phases do not have independent peaks on the diffraction pattern marked "a" in Fig. 1. Four endothermic heat absorption peaks ($T_{h1}=647^\circ$ C, $T_{h2}=736^\circ$ C, $T_{h3}=789^\circ$ C, and $T_{h4}= 933^\circ$ C) were observed on calorimetric curves obtained at a constant heating rate of $20^\circ$/min, corresponding to the successive dissolution of four phases in the alloy. The hardness of the alloy in the quenched state is low and is 216 $HV$. The alloy implements two hardening mechanisms: solid-solution and dispersion.

An increase in the cooling rate (up to $10^6^\circ$/sec) of the same chemical composition alloy leads to the formation of a single-phase amorphous structure with a halo on the diffraction pattern (Fig. 1, b). The amorphous structure of rapidly solidified alloy is a supersaturated solid solution of the alloying elements Ni, Fe, La in aluminum, in which there is no long-range order in the arrangement of atoms. This structure is thermodynamically unstable and under subsequent external influences (thermal, deformation) undergoes relaxation and crystallization. Low thermal stability of amorphous alloys is their distinctive feature, which limits their practical application. Thermal stability of the amorphous structure is retained up to $T=285^\circ$ C, which is established by differential calorimetry. The microhardness of the alloy after rapid quenching is 406 $HV$, which exceeds the hardness of a polycrystalline alloy of the same composition by almost two times. Samples of the same chemical composition, but different in morphological type of structure (polycrystalline and amorphous), were subjected to IPD on Bridgman anvils with twisting angles from $180^\circ$ to six full revolutions. Figure 2 shows typical diffractograms of amorphous (a) and polycrystalline (b) alloys after IPD, $\varphi=360^\circ$. IPD causes dispersion of all phase components in a polycrystalline sample, which is accompanied by a broadening of the diffraction lines and a decrease in their intensity as the degree of deformation increases in comparison with the diffraction pattern of the same sample after quenching. As the degree of deformation increases, the average size of nanofibers decreases from 19.3 to 9.7 nm with an increase in the twisting angle $\varphi$ from $180^\circ$ to $360^\circ$X6, respectively. After deformation with $\varphi=360^\circ$, the parameters of the phase lattices are determined. It is found that the IPD leads to their increase in comparison with the parameters of the lattices of the phase components before deformation. In this case, the phase composition in the specified range of deformation parameters remains unchanged.
Figure 1. Diffraction patterns: $a$-polycrystal, $b$ – amorphous tape; * - Al, 
# – Al$_{11}$La$_3$, ▼ – Al$_{8}$Fe$_{2}$-xNi$_{x}$La, ▽ - Al$_{9}$Ni$_{2}$-$x$Fe, ● – Al$_{11}$La$_3$, ▼ – Al$_{8}$Fe$_{2}$-xNi$_{x}$La, ○ – Al$_{13}$Fe$_4$.

In the amorphous alloy, IPD causes the development of partial crystallization. The X-ray pattern shows intensity peaks formed by the reflection from crystal phases: solid solution of Al and intermetallides Al$_{11}$La$_3$, Al$_{8}$Fe$_{2}$-xNi$_{x}$La, Al$_{9}$Ni$_{2}$-$x$Fe. Their intensity increases with increasing degree of deformation. In the studied range of deformation parameters, crystallization is not complete: the amorphous phase is partially retained. In general, the structure of the alloy is an amorphous nanocrystalline composite with a fragment size of about 10 nm.

As it was shown earlier [1], crystallization in an amorphous alloy under IPD develops according to the scheme: stratification, the formation of a fragmented structure with a fragment size of about 10 nm, partial crystallization at the boundaries of fragments with the formation of nanograins of 3-5 nm in size and the retention of an amorphous core. This "necklace" type structure was observed in samples after the IPD $\varphi=180$-$360^\circ$. Primary crystallization of nanograins with the release of intermetallic compounds at the boundaries of fragments is determined by their enrichment in Ni and La. The method of differential calorimetry shows that the thermal stability of the initial amorphous alloy increases after the IPD, $\varphi=360^\circ$x3. The temperature of the beginning of crystallization when heating an amorphous nanocrystalline structure is $T_{x1}=347^\circ$C, which is 62 ° higher than the temperature of the beginning of crystallization of an amorphous alloy without IPD (Table 1). In contrast to the three-stage crystallization of a hardened amorphous alloy Al$_{83}$Ni$_{7}$Fe$_4$La$_4$ heated in a calorimeter, a single-stage crystallization with an exothermic peak temperature of $T_{p1}=358^\circ$C was observed after the IPD ($\varphi=360^\circ$x3) in it (Table 1). This is probably due to the implementation of partial multiphase crystallization and relaxation in the non-recrystallized amorphous phase at the preliminary IPD.
Figure 2. Diffraction patterns of the alloy after the IPD of 8 GPa, $\varphi=360^\circ$; the initial state is amorphous ($a$) or polycrystalline ($b$); 1 - Al, 2 - Al$_{11}$La$_3$, 3 - Al$_9$Ni$_2$-$\chi$Fex, 4 - Al$_8$Fe$_{2-x}$Ni$_x$La, * - Al$_3$Ni

Comparison of mechanical characteristics of samples was performed based on the results of microhardness measurement after IPD and the complex effect of IPD + FLA (table 2). With an increase in the degree of deformation, a regular increase in microhardness was observed both in amorphous tapes and in polycrystalline samples. This process is primarily associated with the grinding of grain in polycrystals to the nanoscale range. In amorphous tapes, the increase in hardness is due to nanocrystallization with the formation of a multiphase amorphous-nanocrystalline structure, which includes high-strength intermetallicides and a solid solution based on aluminum in the nanocrystalline and amorphous states. In an alloy with both types of primary structure, the density of defects increases sharply, which is one of the factors for increasing the hardness after the IPD. Its maximum values of 706 and 575 HV were obtained for the alloy after the IPD with the degree of deformation $e = 8.3$ ($\varphi=360^\circ$x6) for the primary amorphous and polycrystalline structure, respectively. The hardness of an alloy with a primary amorphous structure remains higher than that of a polycrystalline alloy over the entire range of deformation parameters (Table 2).

Table 1. Phase transformations temperatures of an amorphous alloy during continuous heating.

| Condition   | I stage | II stage | III stage |
|-------------|---------|----------|-----------|
|             | $T_{x1}$, °C | $T_{p1}$, °C | $T_{x2}$, °C | $T_{p2}$, °C | $T_{x3}$, °C | $T_{p3}$, °C |
| Amorphous   | 285     | 296      | 371       | 382       | -          | 393       |
| + IPD       | n=1     | 288      | 302       | 344       | 362        | -          |
| + IPD       | n=3     | 347      | 358       | -         | -          | -         |

$T_{x1}$ – temperature of the beginning of transformation; $T_{p1}$ – maximum heat release temperature

After complex processing, including IPD with $e=5.5$ ($\varphi=360^\circ$) + FLA at $F \leq 20$ j/cm$^2$, we observed an increase in microhardness to 651 HV and 569 HV for the primary amorphous and polycrystalline structure, respectively, compared with the hardness of deformed alloys without IFO (Table 2).
Increasing the fluence to 25 J/cm² reduces the microhardness of the alloy with both types of primary microstructure. This non-monotonic dependence of microhardness on the fluence value is due to the competition of the processes of dispersion hardening and static softening in the FLA. At the first stage of processing at a fluence of 10\( \leq F \leq 20 \) J/cm², hardening processes prevail, at the second stage at 20 < \( F \leq 25 \) J/cm² – static softening processes: recrystallization, accompanied by grain growth, and coagulation of intermetallics.

Table 2. Microhardness of alloy.

| Treatment | Amorphous alloy | Polycrystalline alloy |
|-----------|-----------------|----------------------|
| Initial state | 406 | 216 |
| IPD, 8 GPa | \( \varphi=360^\circ \times 1 \) (e=5,5) | 580 | 492 |
| | \( \varphi=360^\circ \times 3 \) (e=7,0) | 619 | 553 |
| | \( \varphi=360^\circ \times 6 \) (e=8,3) | 706 | 575 |
| IPD 8 GPa, \( \varphi=360^\circ \) + FLA | \( F=10 \) J/cm² | 605 | 522 |
| | \( F=20 \) J/cm² | 651 | 569 |
| | \( F=25 \) J/cm² | 557 | 533 |

\( e \) – true total shear and draft strain, \( F \)-fluence of the FLA.

To determine the stability of the structure and temperature of phase transitions on the samples with both types of structure after complex exposure, calorimetric studies were performed. The results are shown in Table 3. In this work, 2 cycles of heating to the melting point were performed on the samples, taking into account that during the first cycle the sample melts and the effect of complex treatment is removed. During the second heating cycle, samples of both types have the structure of a hardened polycrystalline alloy. Comparison of the DSC curves of the first and second cycles revealed some features in the phase transformations during heating. Four endothermic peaks of heat absorption are caused by the melting of four phase components of the alloy (Table 3). The temperatures of phase transitions fluctuate slightly. The value of the enthalpy \( \Delta H_1 \) and \( \Delta H_2 \) of the first and second cycles differs significantly.

The enthalpy of \( \Delta H_1 \) at the first peak of transformation increases markedly from 8.8 to 15.7 mV×s/mg when comparing the first and second heating cycles, respectively (Table 3). The enthalpy of the second stage of transformation with \( T_p=733^\circ C \) \( \Delta H_2=9.5 \) mV×s/mg during the first heating cycle significantly exceeds the values of \( \Delta H_2=1.6 \) mV×s / mg of the second cycle. Similar dependences of the enthalpy of the 1st and 2nd heating cycles were obtained on samples with a primary amorphous structure after complex treatment of IPD + FLA. As shown earlier, the first peak on the calorimetric curves in the temperature range of 625-630 °C corresponds to the melting of a solid solution of aluminum, the second in the temperature range of 730-740 °C corresponds to the melting of intermetallic \( \text{Al}_1\text{La}_3 \). The change in the enthalpy of \( \Delta H_1 \) and \( \Delta H_2 \) after two heating cycles indicates a greater volume fraction of intermetallic \( \text{Al}_{11}\text{La}_3 \) in samples of both types after complex treatment. In the entire range of the studied processing parameters, an alloy with a primary amorphous structure demonstrates higher hardness values compared to the hardness of an alloy with an initial polycrystalline structure (Table 2). The maximum hardness value of 651HV was obtained after a complex treatment of IPD 8 GPa, \( \varphi=360^\circ + \text{FLA} \), \( F=20 \) J/cm2 in an alloy with a primary amorphous structure, which is 14% higher than the hardness of an alloy with a primary polycrystalline structure. When compared with the hardness of an amorphous alloy after the IPD without IFO, an increase in hardness of 12% was obtained.
Table 3. Phase transformation Temperatures and enthalpy at continuous heating of alloy after complex treatment: IPD 8 GPa, $\varphi=360^\circ +$ FLA 20J/cm.

| Primary structure | Cycle | I peak | II peak | III peak | IV peak |
|-------------------|-------|--------|---------|----------|---------|
|                   |       | $T_{x1}$ | $T_{p1}$ | $\Delta H_1$ | $T_{x2}$ | $T_{p2}$ | $\Delta H_2$ | $T_{x3}$ | $T_{p3}$ | $\Delta H_3$ | $T_{x4}$ | $T_{p4}$ | $\Delta H_4$ |
| Polycrystalline   | 1     | 629,5  | 641,3   | 8,8      | 722,8   | 733     | 9,5      | -        | 786      | 2,9     | 913      | 940      | 3,3      |
|                   | 2     | 625    | 636     | 15,7     | 719,6   | 734     | 1,6      | -        | 790      | 3,8     | 889      | 943      | 3,0      |
| Amorphous         | 1     | 632    | 637     | 13,5     | 732     | 742     | 11,6     | 782      | 787      | 1,9     | 860      | 917      | 9,6      |
|                   | 2     | 626    | 631     | 22,3     | 716     | 730     | 2,2      | 778      | 788      | -       | -       | -       |

$T_{x1}$ - the temperature of the beginning of the transformation, °C; $T_{p1}$ - the temperature of the maximum heat release, °C; $\Delta H_i$ – the enthalpy of the transformation, mV×s/mg; $i$ – the number of the peak from 1 to 4.

4. Conclusion

Thus, the alloy with a primary amorphous structure demonstrates higher hardness values, both for separate (only IPD) and complex (IPD + FLA) treatments. The use of complex processing, including IP + FLA, opens the possibility of forming nanocrystalline high-strength coatings, gradient coatings with variable elastic and strength characteristics, and bulk structures in products of arbitrary shape with a primary amorphous structure. This method of processing is simple, low labor intensity, which makes it relevant to use it for processing amorphous alloys to control their structure and properties.

5. Acknowledgments

The investigations have been fulfilled according to the Federal order № 075-00947-20-00.

6. References

[1] Bakhteeva ND, Todorova EV, Volkov PA, Vasil’ev AL. Thermal Stability of Al–Ni–Fe–La Aluminum Amorphous Alloys. Russian Metallurgy (Metally). 2012, No. 5, pp. 404–414.