The role of the melt properties in the formation of supersaturated nanostructured solid solutions of transition metals in aluminum

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Abstract. Metallographic, X-ray diffraction and electron microscopy were used to study the phase compositions and structure of rapidly solidified Al-alloys with transition metals (Zr, Fe, Cr) subjected to severe plastic deformation by torsion under a high quasi-hydrostatic pressure (HPT). It was established that upon HPT a number and a size of aluminides decrease with increasing in a degree of deformation. For example, the maximum effect of deformation-induced dissolution of the particles is observed in the case where they have a dendritic structure and are about one micrometer in size. Upon HPT the supersaturation of $\alpha$-phase increases by a factor of 2.5. in rapidly solidified Al-Cr and Al-Cr-Zr alloys and by a factor of 10 in rapidly solidified Al-Fe alloys. After HPT all alloys have ultrafine-grained (UFG) Al-based matrix with grain size of 70-200 nm and high hardness of 2 GPa.

1. Introduction

The problem of fabrication of bulk ultrafine-grained (UFD) alloys using techniques of severe plastic deformation (SPD) has attracted great international attention in recent years. High pressure torsion (HPT) is the SPD technique that is used to produce nanostructured Al alloys with submicron or nanosized grains [1].

The development of casting technologies based on melt quenching methods led to the design of new structural materials such as granulated alloys [2].

A new class of heat resistant Al alloys with a high content of transition metals (TM) such as Cr, Zr, Fe, Mn has come to use. The most important structural factor responsible for the realization of high properties in such materials is formation of supersaturated solid solutions of TM in Al [2]. The formation of anomalously saturated solid solutions is possible only upon significant under cooling of the melt. The structure and properties of semiproducts prepared from granulated alloys are conventionally improved by increasing in the melt cooling rate. This is connected with certain methodical difficulties.

The detailed study of the regularities of crystallization of such materials and modern concepts on the micro-inhomogeneous structure of metallic melt allowed researchers to outline the principles of interrelations between the liquid and solid states. It promoted to develop efficient regimes of heat-time treatment (HTT) of melts, which would allow one to obtain anomalous structural states in more massive casts [3].

The aim of this study is to investigate phase and structure transformations upon different external actions in liquid and solid Al alloys with TM (HTT of melts, rapid quenching and HPT).
2. Experimental
The binary and ternary aluminum alloys with transition metals (TM=Zr, Cr, Fe) were used as objects of the investigation. These materials were cast by two different methods as ingots and disks to produce a wider spectrum of structures and phase compositions.

The ingots were cast into a steel mold; the cooling rate was \( V \leq 10^2 \) K/s and the overheating above the liquidus temperature \( \Delta T \) of 200 K. The disks with a diameter of 80 mm and a thickness of 0.6 mm were produced using the method of centrifugal casting with two-sided cooling. In this case the cooling rate of a melt \( V \) was of \( 5 \times 10^3\) - \( 10^4 \) K/s and the overheating changed from 100 to 450 K.

Specimens of a diameter of 10 mm (which were cut from the cast disks) were subjected to SPD using rotating Bridgman anvils at a high quasi-hydrostatic pressure \( P \) of 5 GPa (HPT) at room temperature. The number of anvil revolutions was varied from 0.5 to 10 (equivalent to logarithmic true strain \( \varepsilon \) of 3.8-6.7). Structural examinations were performed by the optical and electron microscopic methods using NEOPHOT -2 and JEM -200 CX microscopes. The size of structural constituents in the cast alloys was estimated using computer methods of quantitative metallography. The sizes of matrix grains and aluminides in the deformed specimens were calculated using the bright- and dark-field electron micrographs. The results were statistically processed, and histograms were plotted using a computer program.

The lattice parameter of the matrix and the phase compositions of the specimens were determined in the Co K\(_\alpha\) radiation using a DRON 3 diffractometer. The profile, width, and center of gravity of the X-ray \((331)\alpha\) diffraction lines were calculated using a PROFILE computer program. The samples were annealed in a muffle furnace at 100 to 450 °C for 0.5...6.5 h. The samples were cooled after annealing in air.

3. Results and discussion
The melts of Al alloys with TM have a close physical origin and are characterized by strong particle interaction in spite of different phase diagrams (the Al-Fe is eutectic, but Al-Cr, Al-Zr and Al-Cr-Zr are peritectic systems).

Figure 1 shows a typical temperature dependence of the kinematic viscosity of liquid hypereutectic or hyperperitectic Al-based alloys with TM, which were obtained in the modes of heating and subsequent cooling.

![Fig. 1 Typical temperature dependence of kinematic viscosity of Al-based alloys with TM](image)

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The given melts have a high values of viscosity and density and retain their micro-inhomogeneous state in a wide range of overheating above the liquidus temperature \( \Delta T=400\text{-}500 \) K. The temperature dependences of their structure-sensitive properties are featured by the presence of a hysteresis and
anomalous increase in the viscosity upon heating near the temperature of the melt transition into a homogeneous state ($T \leq T_{\text{hom}}$). These peculiarities of liquid alloys were employed to purposefully monitoring the structure of rapidly quenched alloys by means of different time-temperature treatments of the melt.

For instance, the overheating up to the temperature of the anomalous viscosity growth ($T \leq T_{\text{hom}}$) and rapid quenching of Al—(1.5—3%) Zr alloys resulting in the formation of the dispersed (2—5\(\mu\)m) metastable Al$_3$Zr aluminides with a dendrite-like cubic structure of the L1$_2$ type (Fig. 2a).

Another task was to suppress the growth of primary aluminides in the Al—(2—5%)Fe alloys and to produce the (Al+Al$_6$Fe) metastable quasi-eutectic. It has come to realization only after overheating of the melt above $T_{\text{hom}}$ and a quenching with a cooling rate of $10^4$ K/s (Fig. 2b).

![Fig. 2 Structure of the rapidly quenched alloys: (a) Al—Zr; (b) Al—Fe; (c) Al-Cr-Zr.](image)

Combination of HTT ($T \leq T_{\text{hom}}$) and rapid quenching of the melt ($V=10^4$ K/s) in the binary Al—3% Cr and the ternary Al-Cr-Zr (Cr+Zr=3.6%) alloy results in the formation of faceted Al$_7$Cr aluminides with a monoclinic lattice 5—10 \(\mu\)m in size, dendrites of Al$_3$Zr metastable phase (2—5 \(\mu\)m), and grains of the Al-based solid solution (Fig. 2c).

The metastable alloys produced by the rapid quenching were subjected to HPT. Such action gives a rise to three processes: formation of UFG structure, deformational dissolution of the TM aluminides, and formation of supersaturated Al solid solution of TM.

The formation of UFG structure with the crystallite size of 70 nm (for ternary alloys) and 150—200 nm (for binary compositions) proceeds through the stage of a mixed structure and terminates at high logarithmic true strains $\varepsilon \geq 4.5$—6. Such structural state provides high hardness values of 1.8—2.5 GPa.

The kinetic and mechanism of dissolution of the TM aluminides depend on their size, morphology, and crystalline structure. In particular, the metastable Al$_3$Zr aluminides with a cubic lattice L1$_2$
dissolve in the Al matrix at $\varepsilon \geq 4.5$. The metastable $\text{Al}_6\text{Fe}$ aluminides with an orthorhombic lattice and the $\text{Al}_7\text{Cr}$ aluminides having a monoclinic lattice dissolve at $\varepsilon \geq 5.1$ and at $\varepsilon \geq 5.8$ respectively. Deformational dissolution of the intermetallics results in an additional alloying of the Al matrix.

It is found that the complex treatment of the alloys in liquid and solid states increases a degree of supersaturation of the Al solid solution with respect to the equilibrium state by a factor of 3 and 7 for the Al-Zr and Al-Cr alloys, respectively, and by the order of magnitude for the Al-Fe compositions. The formation of supersaturated solid solutions upon HPT provides an additional hardening of the material owing to the solid-solution strengthening, increases the thermal stability, and preserves a high hardness of the UFG structure.

It is established that upon heating the UFG materials, the simultaneous proceeding with recovery ageing compensates the loss of strengthening. This is due to the effects of dispersion hardening and of precipitation of disperse secondary phases upon the matrix ageing. Such structure peculiarly moves the process of intense growth of the grains toward the temperatures $T \approx 0.5 T_i$, which is 0.2—0.3$T_i$ higher than for other UFG Al-based alloys after the similar deformation.

4. Conclusion

The structural and phase transformations occurring upon rapid crystallization and severe plastic deformation in Al-TM alloys were studied.

It was established that the combined treatment of alloys in liquid and solid states is resulted in the formation of UFG structure.

The results of this work present the opportunity to suggest practical recommendations on the optimization of the regimes of melt quenching and subsequent HPT, aiming at the achievement of high service properties of the given nanomaterials.

References

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