Abstract

Transition metal silicides based on Fe-Ni-Si system have been identified as highly promising candidates for diverse fields of application, which stems from their excellent magnetic/electrical as well as structural properties. Mechanical alloying (MA), a low temperature solid-state processing method, bypasses the processing difficulties of conventional methods and provides an attractive alternative route for the synthesis of both amorphous and intermetallic silicides. In addition, the feasibility of producing solid solution and intermetallics in nanocrystalline state has widened the scope of MA. The objective of the present investigation is to study the synthesis, mechanism of formation and thermal stability of nanocrystalline silicides in Fe-Ni-Si system obtained by MA.

Solid state reactions induced by mechanical alloying (MA) of elemental blends of Fe, Ni and Si have been studied over the entire composition range of binary Ni-Si, Fe-Si as well as ternary Fe-Ni-Si systems. During MA in Ni-Si, Fe-Si and Fe-Ni-Si systems, the silicides and solid solution start to form when the crystallite size of Ni/Fe drops to the nanometer regime (~20-25nm), while the Si remains much coarser in size (≥100nm), which can be attributed to a significant increase in effective diffusivity below a critical crystallite size (~20nm). The results, obtained by MA in the above mentioned systems, clearly suggests that only amorphous or congruent melting phases form while the formation of non-congruent melting phases is bypassed in the nanocrystalline state (~10-25nm). In Ni-Si system the phase fields in the nanocrystalline state after MA are found to be Ni(Si), Ni(Si)+$Ni_{31}Si_{12}$, $Ni_{31}Si_{12}$+Ni_2Si, Ni_2Si+ NiSi and NiSi+Si in the composition ranges of 0-10, 10-28, 28-33, 33-50 and 50-100at.%Si, respectively. The phase fields obtained in the nanocrystalline state during MA in Fe-Si system are Fe(Si), Fe(Si)+ε-FeSi and ε-FeSi+Si in the composition ranges of 0-25, 25-50 and above 50at.%Si, respectively. In addition, an allotropic transition from fcc to hcp Ni(Si) solid solution (up to 10at.%Si) accompanied with a volume expansion of 8.6% has been observed, which is triggered when fcc Ni(Si) reached a critical crystallite size of 10nm. Amorphization of Fe(Si) has been observed below a crtical crystallite size of ~11nm and above a critical lattice strain ~1.28%.

Abstract

The underlying solid state reaction and the mechanism of formation of both stable and metastable phases during MA has been explained based on the concepts of atomistic, thermodynamic and kinetic considerations. The thermodynamic calculations, based on Miedema's semi-empirical model for enthalpy calculation and the contribution of interfacial energy arising due to nanocrystalline nature of product phase, can explain the stability of metastable phases in nanocrystalline state synthesized by MA. The predicted phase fields obtained from modified effective free energy calculation, based on the concepts of stability of the amorphous/metastable solid solution against the homogeneous/heterogeneous nucleation of the second phase in the concentration gradient field, are quite close to those obtained during MA in Ni-Si and Fe-Si system. Calculations based on atomistic model (mechanical instability) show that a 37% reduction in tetragonal shear modulus and a negative pressure of about 8.7GPa has been generated at the onset of fcc to hcp Ni(Si) transformation. A ~33% reduction in rhombohedral shear modulus occurs at the onset of amorphization of bcc Fe(Si). The observed MA kinetics of Fe-25at.%Si, calculated based on modified iso-concentration contour migration model, is equivalent to that by volume diffusion at an effective temperature ~840K which correspond to ~$0.5T_L$ (T_L is liquidus temperature).

The thermal stability of both stable and metastable nanocrystalline silicides against significant grain growth and phase transformation to equilibrium state has been studied because such changes may consequently result in the loss of some unique properties of non-equilibrium materials. Thermal treatments of nanocrystalline silicides in Fe-Ni-Si system have led to the formation of equilibrium noncongruent melting phases in most of the compositions studied. The crystallite size of these noncongruent melting compounds is well above 100nm at the stage of their evolution, which suggests that grain growth is very fast for these phases, and probably they are stable only in the bulk state. The defect induced hcp Ni(Si), transformed back to the equilibrium fcc Ni(Si) at 573K when its crystallite size reached about 20nm and when the lattice distortion in fcc Ni(Si) reached a minimum. Amorphous phase in Fe-Si (up to 25at.%Si) and Fe-Ni-Si system ($Fe_{75-x}Ni_xSi_{25}$ and $Fe_{67-x}Ni_xSi_{33}$, x=10-40) shows two-step crystallization process. The 1st crystallization process leads to formation of equilibrium stable compound Fe_3Si, while in the 2nd stage the residual amorphous phase transforms to metastable hexagonal structure in case of Fe-Si system or $(Ni,Fe)_2Si$ for Fe-Ni-Si system. The lattice distortion in nanometer-sized

crystallites in comparison to the equilibrium configuration appears to act as self-obstacle in controlling the grain growth of nanocrystalline materials. It is also proposed that the interfacial energy of metastable and stable phases in the nanocrystalline state plays an important role in controlling the grain size stability of nanocrystalline materials.