Microstructure Evolution and Mechanical Properties of Ni-5Pt Alloy during Cold Rolling

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Abstract: Nickel-platinum (NiPt) alloy sputtering target was used in semiconductor industries for the formation of Ni-Pt-silicide to realize the contact and interconnection functions. The microstructure evolution of a Ni-5Pt alloy was studied during the cold-rolling process, and the mechanical properties were also studied. The results showed that, during the cold-rolling process of the Ni-5Pt alloy, the microstructure evolved from dislocation tangles to dislocation walls, and then elongated subgrains with both dislocation walls and low grain boundaries, finally became elongated grains with sharp grain boundaries. The grain refinement was mainly controlled by the accumulation, annihilation and rearrangement of the dislocations. The microhardness of Ni-5Pt increased with rolling reduction, which was consistent with the variation in strength. The increase in strength of the Ni-5Pt alloy was believed to be primarily because of the cold rolling-induced increase in dislocation density and the grain refinement effect.

Key words: metal materials; sputtering target; NiPt alloy; cold rolling; dislocation; grain refinement

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Ni-5Pt 合金在冷轧过程中的结构演变及力学性能

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摘　要：镍铂合金溅射靶材在半导体工业中用于制备镍铂硅化合物，实现接触和互连的功能。Ni-5Pt 合金在冷轧过程中的结构演变及力学性能进行了研究。结果表明，Ni-5Pt 合金在冷轧过程中其微观演变为从位错缠结到位错墙，再到含位错墙和小角晶界的拉长亚晶粒，最后形成了具有明锐晶界的拉长晶粒。晶粒细化主要是受位错的聚集、湮灭和重排所导致。Ni-5Pt 的显微硬度随着轧制变形量的增加而增加，与强度的变化一致。Ni-5Pt 强度的增加可主要归因于冷轧诱导的位错密度增加和晶粒细化效应。

关键词：金属材料；靶材；NiPt 合金；冷轧；位错；晶粒细化

Nickel silicide is extensively used in advanced devices such as complementary metal oxide semiconductors (CMOS) because of its low resistivity and low silicon consumption[1-2]. Recently, platinum was incorporated into Ni silicide in order to improve the thermal stability[3]. Usually in semiconductor manufacturing, Ni-Pt films are deposited onto the silicon device by magnetron sputtering via the

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corresponding Ni-Pt sputtering target, and then react with the silicon at certain temperatures to form Ni-Pt-silicide in order to realize the contact and interconnection functions. In fact, the quality of the sputtering target has a great impact on the microstructure and properties of the corresponding thin films[4-5]. Some researchers studied the properties and phase transformation in Ni-Pt alloys[6-9]. Greenholz et al. investigated the order-disorder transition of an Ni-Pt alloy with high-temperature X-ray measurements and found it was a first-order phase transformation[6]. The transition of Ni-Pt alloy from a disordered to an ordered state can be attributed to two mechanisms: 1) the nucleation of ordered zones and their growth are dominant at low temperature; and 2) nucleation- and-growth kinetics play a leading role at high temperature[7].

Generally, the basic requirements for a sputtering target are high purity (≥99.99%), and fine and uniform grain size distribution in the plane and along the thickness of target. The typical method to refine the grain size of the target is plastic deformation, such as rolling, forging or extrusion. Hui et al. decreased the grain size of a Ni-Pt target in the range of 200~300 μm using alternate hot rolling in straight and crosswise directions[10]. However, there were few studies investigating the relationship between deformation, such as cold rolling, on the microstructure and mechanical properties of Ni-Pt alloys, especially alloys with low Pt content.

In this work, the microstructure evolution of a Ni-Pt alloy during cold rolling has been studied and the mechanical properties including micro-hardness and tensile properties are also investigated and discussed.

1 Experimental

The alloy was prepared from high purity ($\omega \geq$ 99.99%) Ni and Pt plates. The Ni and Pt plates were weighted by the required composition (mass fraction) of 95% Ni and 5% Pt (Ni-5Pt), and then put into a vacuum induction furnace and cast into an ingot. The ingot was cold rolled at room temperature with a pass deformation (thickness reduction) of 5% until the total deformation achieved was 80% with a final thickness of 6 mm. Samples were taken when the deformation was 10%, 35%, 50% and 80%. Structure characterization and mechanical testing of all samples were carried out on the longitudinal section (rolling direction - normal direction plane, RD-ND plane). For comparison, as-cast samples were also prepared.

Microstructure observation was first carried out using a metallographic microscope. Then a Tecnai G2-TF30 electron transmission microscope (TEM) operating at an accelerated voltage of 300 kV was used to observe the microstructures in detail. TEM specimens were punched into 3 mm diameter discs and mechanically polished to a thickness of 50 μm, and then the central region of the discs was thinned to 20 μm with a GATAN 656 dimple grinder. Finally, a Gatan Model 691 precision ion polishing system was used to polish all samples; the operating angle of the ion guns was ±8° with an accelerated voltage of 4.5 keV. A Rigaku-D/max 2400 X-ray diffractometer (12 kW) with Cu K_{α} radiation was used to determine the phase constitution. A hardness test was carried out on the RD-ND plane with a load of 300 gram and a dwell time of 15 sec using a HXS-1000A micro-hardness tester. For each measured plane, at least 5 points were measured to calculate the mean value of micro-hardness. Dog-bone tensile specimens with a gauge length of 15 mm and gauge width of 3 mm were cut from the RD-ND plane by spark cutting and then polished mechanically. Tensile tests were conducted on an AG-IC10KN universal tensile-testing machine at a constant crosshead speed of 1.67×10^{-5} m/s with the tensile axis parallel to the rolling direction (RD). At least three repeated tensile samples were tested for each deformation state. Fracture surface observations were conducted using an SPM-S3400N scanning electron microscope (SEM).

2 Results

Fig.1 presents the XRD patterns of the Ni-5Pt alloy in the as-cast and cold-rolling states. It can be seen that the alloy is composed of a face centre cubic (fcc) Ni-based solid solution and no phase transition occurs during subsequent cold rolling. The widths of the diffraction peaks in the deformed specimens broaden as compared with those of the as-cast sample and increases slightly with deformation, suggesting the grain refinement and accumulation of strain during the cold-rolling process. The preferred orientation of the Ni-5Pt alloy changes gradually from (111) to (200) until reaching the (220) plane with high deformation.

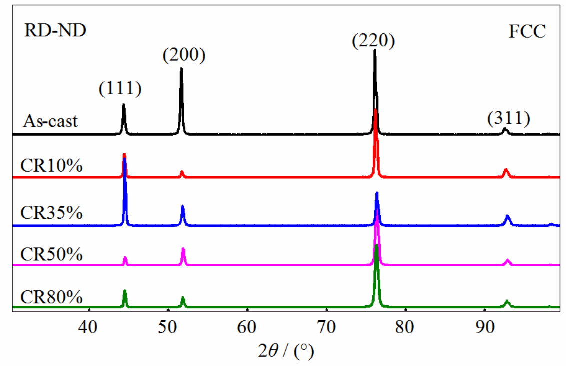
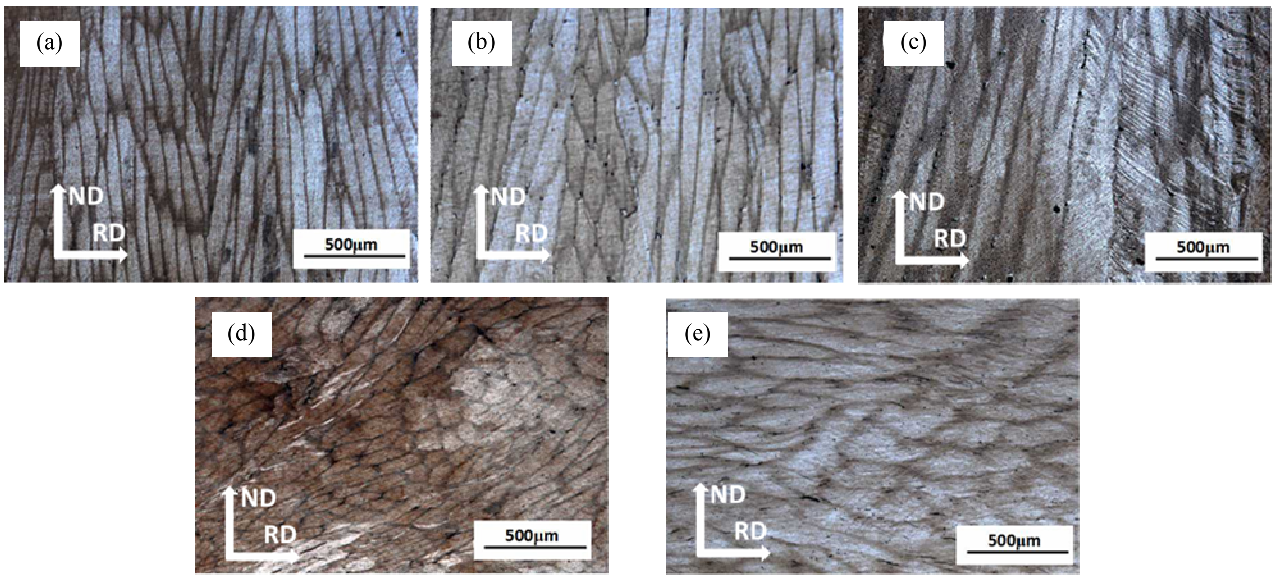


Fig.1 XRD patterns of Ni-5Pt alloy in as-cast and cold-rolled states

图 1　Ni-5Pt 合金铸态和冷轧后的 X 射线衍射图谱

Fig.2 shows the optical microstructure of the Ni-5Pt alloy in the as-cast and cold-rolled states. The as-cast Ni-5Pt alloy exhibits a columnar grain structure and the growth direction of the columnar grains is almost perpendicular to the RD (Fig.2 (a)). No significant change can be seen in the alloy with 10% deformation (Fig.2 (b)). As the deformation increases to 35%, the alloy exhibits a wavy and not well- delineated state inside the grains and the grain boundaries tends to incline along the RD. Some slip bands appear in some grains, suggesting non-homogeneous deformation behavior at this deformation stage (Fig.2(c)). When the deformation increases to 50%, the grains tend to be exquiaxed and almost all grains rotate along the RD (Fig.2 (d)). When the deformation achieves 80%, the grain boundaries become parallel to the RD, and both grain interior and grain boundaries change to a diffused state, implying severe plastic deformation (Fig.2 (e)).

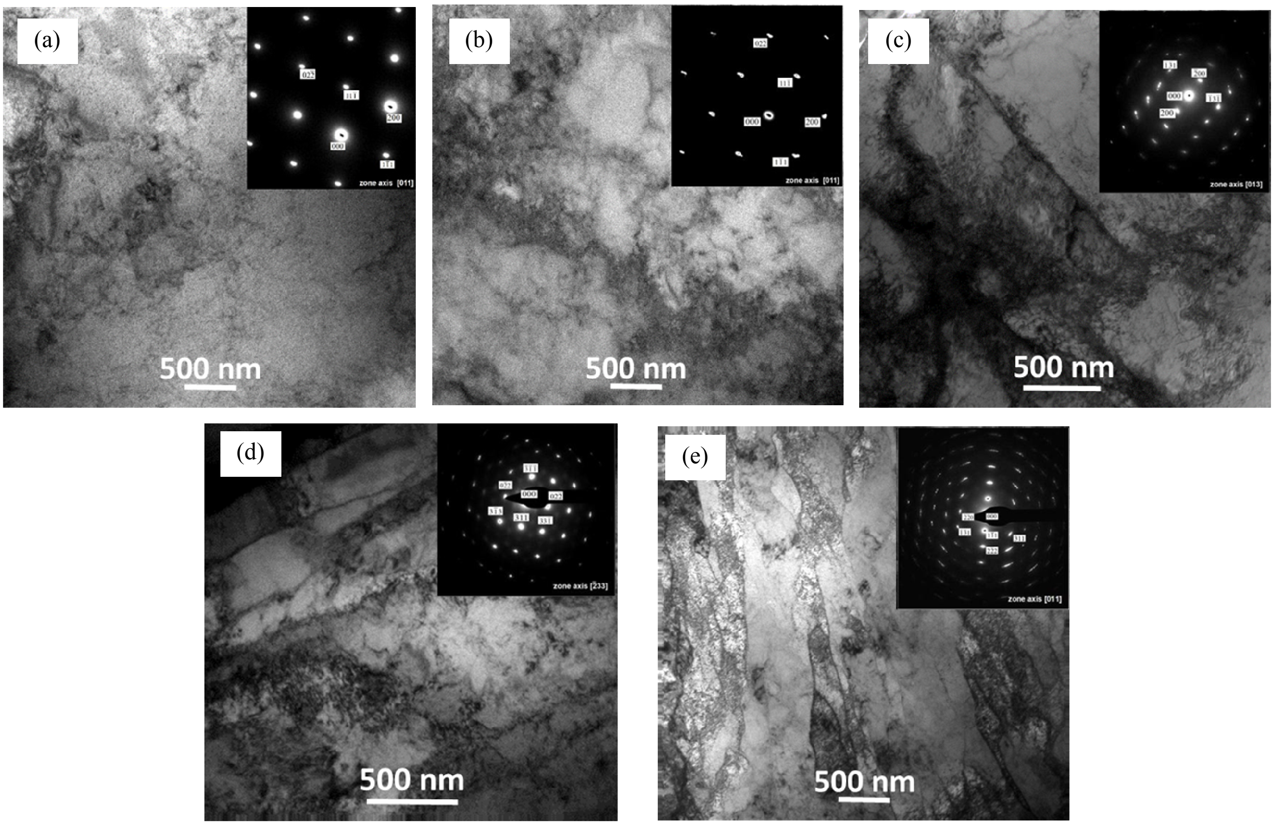


(a). As-cast(铸态); (b). Cold rolled 10%(冷轧 10%); (c). Cold rolled 35%(冷轧 35%); (d). Cold rolled 50%(冷轧 50%); (e). Cold rolled 80%(冷轧 80%)

Fig.2 Optical microstructure of Ni-5Pt alloy in as-cast and cold-rolled states

图 2　Ni-5Pt 合金铸态和冷轧后的光学显微结构

Due to the limited resolution power of optical microscopy, TEM was used to further investigate the structure of the deformed alloys. Fig.3 shows a typical bright-field TEM image and the corresponding selected-area electron diffraction (SAED) patterns of the Ni-5Pt alloy in the as-cast and cold-rolled states. As shown in Fig.3 (a), the as-cast Ni-5Pt alloy with a large, columnar grain structure shows almost no dislocations within the grain, and the SAED also indicates no misorientations inside the grain. When the alloy is cold rolled with 10% deformation, some dislocation tangles appear and the corresponding SAED also shows minor misorientations, suggesting the formation of low grain boundaries inside the grains (Fig.3(b)). When the alloy is further deformed to 35% (Fig.3(c)), dense dislocations appear and dislocation walls form. Correspondingly, the SAED shows some small arcs, indicating the existence of high-angle grain boundaries. When the alloy is cold rolled with 50% deformation, it can be seen that the typical micro-structures are elongated band grain structures with low dislocation densities, and both sub-grain boundaries and dislocation walls co-exist. The grain refinement during cold rolling is obvious as illustrated by the SAED, which gradually transforms into diffraction rings with deformation. When the reduction level achieves 80%, the width of grains and dislocation density further decrease, as compared with Fig.3(d), and the boundaries become sharp and distinct (Fig.3(e)). New grain boundaries form through the accumulation, annihilation and rearrangement of dislocations, which gradually reduces the width of the original grain structure[11].



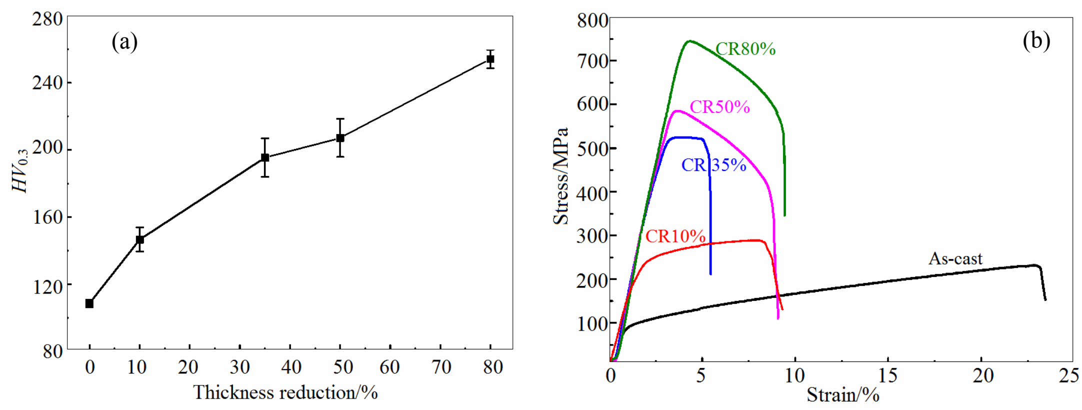
(a). As-cast(铸态); (b). Cold rolled 10%(冷轧 10%); (c). Cold rolled 35%(冷轧 35%); (d). Cold rolled 50%(冷轧 50%); (e). Cold rolled 80%(冷轧 80%)

Fig.3 TEM micrographs and selected-area electron diffraction (SAED) patterns of as-cast and cold-rolled Ni-5Pt alloy samples

图 3 Ni-5Pt 合金铸态和冷轧后的透射电镜图像和选区电子衍射图谱

The mechanical properties of the Ni-5Pt alloy with cold-rolling reduction are shown in Fig.4. Fig.4(a) shows the hardness of the Ni-5Pt alloy in as-cast and cold-rolled states. The hardness of the as-cast alloy is 108.6±2.2. The hardness increases with deformation and that of the Ni-5Pt alloy is 254±5.5 at 80% deformation, which is 2.3 times greater than that of the as-cast counterpart. Tensile engineering stress-strain curves of the Ni-5Pt alloy are shown in Fig.4 (b). The as-cast alloy shows good plasticity and its elongation is 23.6±5.5%. However, its yield strength (0.2% offset) and ultimate tensile strength (UTS) are only 84.5±5.8

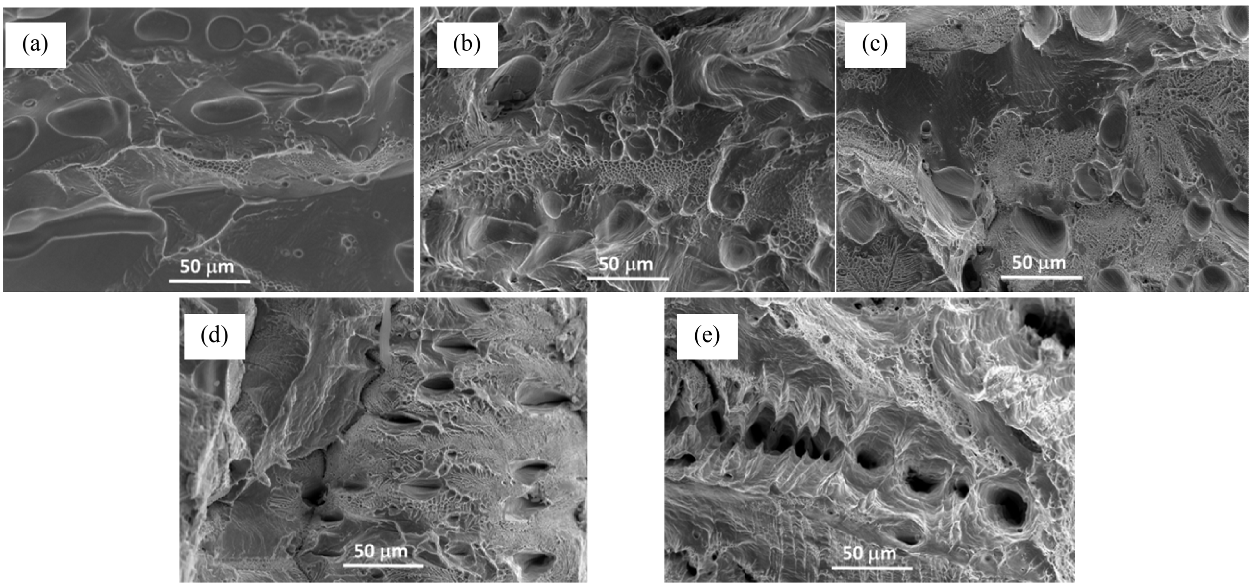
and 238.6±14.9 MPa, respectively. With increasing deformation, both the yield strength and UTS increase rapidly. The yield strength and UTS of the sample with 80% deformation are 671.6±23.7 and 736.9±8.5 MPa, respectively. At the same time, the alloy shows reduced ductility with deformation. The elongation of the alloy with 10%, 35%, 50% and 80% deformation is 9.2±1.6%, 3.9±0.5%, 3.8±0.2% and 4.5±0.3%, respectively.



(a). Microhardness (显微硬度); (b). Representative engineering stress-strain curves (应变-应力曲线)

Fig.4 Mechanical properties of Ni-5Pt alloy with rolling reduction　图 4　不同轧制变形量下 Ni-5Pt 合金的力学性能

Fig.5 presents SEM images of the fracture surfaces of Ni-5Pt. For the as-cast sample, the fracture surface shows a heterogeneous microstructure (Fig.5 (a)). Some large, smooth pores with a size of 10~50 μm and a band of numerous very fine dimples with a mean size of 2.7±1.1 μm can be seen in Fig.5 (a). With deformation to 10% thickness reduction, dislocation slipping traces can be found in the large pores and more areas with fine dimples emerge (Fig.5 (b)). With increasing deformation, numerous dimples become spread across the surface and the whole surface shows a homogeneous microstructure (Fig.5(c)~(e)).



(a). As-cast(铸态); (b). Cold rolled 10%(冷轧 10%); (c). Cold rolled 35%(冷轧 35%); (d). Cold rolled 50%(冷轧 50%); (e). Cold rolled 80%(冷轧 80%)

Fig.5 SEM images of fracture surfaces of Ni-5Pt alloy in as-cast and cold-rolled states

图 5　铸态和冷轧态 Ni-5Pt 合金断裂面的扫描电镜图像

3 Discussions

3.1 Microstructure evolution during cold rolling

In the present work, an as-cast Ni-5Pt alloy was cold rolled up to 80% reduction in thickness. The XRD pattern (Fig.1) and optical microstructure (Fig.2) show that during deformation the Ni-5Pt alloy was composed of an fcc solid-solution phase, showed a {110} type texture and almost all grains rotated along the rolling direction finally during the rolling deformation. This phenomenon is frequently found in fcc metals during rolling deformation[12]. At first, the as-cast Ni-5Pt alloy showed almost no defects inside the grains (Fig.3(a)). With increasing deformation during cold rolling, the dislocations moving on some slip planes curved when they met obstacles such as forest dislocations and the dislocation densities there increased accordingly, creating dislocation tangles (Fig.3(b)). When the dislocation density achieved a critical value, these dislocations were annihilated and rearranged into dislocation walls, and more and more dislocation tangles were created among the dislocation walls (Fig.3(c)). As deformation further increased, the dislocation walls subdivided the original grains into smaller pieces and some dislocation walls also became low grain boundaries (Fig.3 (d)). When Ni-Pt was cold rolled to 80% reduction in thickness, the microstructure was composed of almost all elongated grains with sharp grain boundaries and the dislocation density further decreased as compared with a 50% reduction. The dislocation slips manipulated the cold-rolling deformation process and facilitated the grain refinement of the Ni-5Pt alloy.

3.2 Relationship between microstructure and mechanical properties

The microstructure demonstrated in the present study sheds light on the mechanical behaviour observed for the Ni-5Pt alloy with cold rolling. The microhardness increased with rolling reduction, which is consistent with the variation in yield strength and UTS (Fig.4). The elongation, as expected, decreased dramatically after cold rolling. The decrease in elongation is affected by a hardening effect involving the vartation of defects such as dislocation density[13]. The elongation and strength of the 80% reduced sample were higher than with the 50% reduction, which can be attributed to the finer grain size and lower dislocation density. The fracture surface (Fig.5) revealed typical dimple-type fractography in all samples. With increasing reduction, the fracture surface became homogeneous, suggesting the development of a homogeneous microstructure after cold rolling. Since no phase transformation occurred in the present work, these mechanical properties can be attributed to defects (especially dislocation in present study), texture, grain size, etc.[14]. The increase in strength is believed to be primarily because of the cold rolling-induced increase in dislocation density and the grain refinement effect.

Further work such as: 1) adding an annealing treatment to increase elongation with little loss of strength; and 2) using the Ni-5Pt alloy as a sputtering target to make a thin film and investigating the relationship between the thin films and sputtering target, is necessary to gain a deeper understanding of the applications of Ni-Pt alloys.

4 Conclusions

The grain refinement and mechanical properties have been studied on a cold-rolled Ni-5Pt alloy. Conclusions are drawn as follows:

1) During the cold-rolling process of the Ni-5Pt alloy, the microstructure evolved from dislocation tangles to dislocation walls and then elongated subgrains with both dislocation walls and low grain boundaries, finally becoming elongated grains with sharp grain boundaries. The grain refinement was mainly controlled by the accumulation, annihilation and rearrangement of the dislocations.

2) The microhardness of Ni-5Pt increased with rolling reduction, which is consistent with the variation in yield strength and UTS. The increase in strength of the Ni-5Pt alloy is believed to be primarily because of the cold rolling-induced increase in dislocation density and the grain refinement effect.

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