Structure Changes and Formation Of Bunsenite (NiO) at Recrystallization Of Electrolytically Deposited Ni-Mn-SLayers

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The structure of the electrolytically deposited Ni-Mn-S layers was investigated after annealing at 450 °C in air. The stability of the layers with various preferred orientations is different and was related to the amount of NiO (Bunsenite) in the layer. The <100> preferred orientation has the highest affinity to the formation of NiO. The degree of the preferred orientation, obtained through the texture index TI, is of special importance. The dynamics of the NiO formation shows that the maximum amount of NiO is formed in the first 10 hr of the heat treatment. In addition to the texture, special criteria for the degree of recrystallization processes are the domain sizes and microstrains. The amount of NiO formed is related to the stability of the initial texture. The formation rate of the NiO is reduced with each structural change. These results lead to the conclusion that the information about the changes in the texture and microstructure may lead to a better understanding of the recrystallization process. This may facilitate the understanding of the mechanism and the concrete problems in the practice.

As reported earlier, electrolytic growth of nickel layers from sulfamate electrolytes, with some of the additives containing sulfur, was investigated.^{1,2} The properties of the layers, such as microhardness, residual stress, wearing quality and ductility depend on the deposition conditions and the current density. It is known that applications of these layers are possible at temperatures lower than 260 °C. Different parts of the tools (*e.g.*, gas laser and dies to cast zinc and zinc alloy), cannot be prepared by current electrolytic deposition techniques.³⁻⁷ That is why it is necessary to improve the thermal stability of the layers for general interest. The results of other investigators⁸⁻¹¹ show that this problem can be solved by using Ni-Mn and Ni-Mn-S layers, where the Mn content should not be more than one wt percent. To date, the studies have been focused mainly on the effect that the formation



Pig. 1—X-ray diffraction patterns showing the increase in NiO content as a function of texture: Samples 1 and 3, <100> texture, 3830 and 2020 counts (arbitrary units); Samples 13 and 15, <110> texture, 190 and 150 counts.





conditions influence the tensile strength and the hardness characteristics. The possible influence of the phase content on the plasticity has been mentioned in only one of the references¹¹ and no evidence is presented to support this possibility.

Inasmuch as our previous investigations¹² of the electrolytic deposits made it clear that the structure that forms under certain growing conditions is of particular importance for the properties of the deposited layers, effort was made to clarify its role in the Ni-Mn-S systems. By employing statistical regression analysis of the explicit correlation between some of the structural parameters studied, the quantity of the incorporated micro-impurities and the microhardness has been found.^{13,14} It has been established for the first time that the values of the texture index could be used as an indication of the status of the electrolytically deposited layers. One of the major requirements for this type of layers is preservation,

or minimum alteration in their basic properties, over a large temperature range. That is the reason for our investigations of the properties such as morphology and structural characteristics at 450 °C as well.¹⁵ It has been established that in some sample groups, the extent of the recrystallization process is different, which is expressed by the texture and its texture index. On the basis of this research, it may be assumed that by varying the structure of the deposited layers, it is possible to prepare systems exhibiting different behavior after heat treatment.

To clarify the causes of these differences, the aim of this study was to investigate structural changes, the possibility for eventual formation of new compounds during the high-temperature recrystallization process, and the probable factors on which it depends.



Fig. 3—Relationship between NiO content and change of microstrain $\Delta \varepsilon$ during heat treatment.

Experimental Procedure

Samples investigated were in the form of foils about 50 μ m thick. They were deposited from a typical nickel sulfamate electrolyte: 35 g/L boric acid and 80 g/L nickel (3 g/L as NiCl₂ · 4H₂O), pH 3.6 to 4.0, CHT 0.1 resp. 0.4 g/L and manganese 5 g/L. Deposits were formed using direct current (DC) and pulsed current (pulse time 10 msec, contact-speed 0.2 to 100 percent, average current density D_k, 1 to 5 A/dm², pulse current density I_p: 10 to 50 A/dm²). Manganese content was found by ASS, sulfur by combustion in oxygen; Vickers microhardness was determined with a load of 100 p (HV 0.1). Ductility was observed by a mechanical bulge tester (ball diameter 8 mm, speed 7.3 mm/min), according to DIN 50102.

X-ray investigations were performed with a diffractometer, equipped with an open asymmetric Eulerian cradle for stress and texture measurements. The measured intensity scale of the chosen reflections in Bragg-Brentano geometry was used in correlation with specialized software. As a standard profile, a corresponding profile of an electrodeposited nickel layer from a sulfamate electrolyte without additions after a heat treatment at 690 °C for two hr was used. The splitting of the line profile was done with the help of the Voigt analysis. By this method, it is assumed that the Cauchy component of



Fig. 4—Relationship between NiO content and change of microstrain $\Delta \varepsilon$ only for samples not showing change of <100> texture during heat treatment.

Table 1
dence of Amount of NiO from Deposition
nditions, Layer Composition & Texture

Components Before & After Heat Treatment

Depen

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	Experimental				Layer Composition				
	No.	Dk	Ір	CHT		S	Mn	Mn:S	0
			A/dm ²	g/L	I	opm	wt %		ppm
	01	2.5	DC	0.1		150	0.14	9.3	150
Α	02	5.0	DC	0.1	:	230	0.29	12.6	303
	03	1.0	50	0.1		140	0.08	5.7	171
	04	1.0	50	0.4	:	280	0.10	3.6	46
B1	05	1.0	10	0.4	:	240	0.09	3.8	67
	06	1.0	50	0.4	:	280	0.11	3.9	81
	07	5.0	DC	0.4		600	0.45	7.5	160
	08	5.0	10	0.4	:	340	0.39	11.5	117
B2	09	2.5	50	0.4	:	250	0.31	12.4	114
	10	5.0	50	0.4	:	320	0.46	14.4	419
	11	2.5	50	0.4	:	290	0.44	15.2	241
	12	5.0	DC	0.4		510	0.61	12.0	412
	13	5.0	50	0.4		400	0.53	13.3	500
С	14	2.5	50	0.1		180	0.18	10.0	141
	15	5.0	50	0.1	:	200	0.37	18.5	211
	16	2.5	DC	0.0		60	0.45	75.0	263

Texture Components						
Initial Textu	re	- End Text	End Texture			
components	ΤI	components	TI	(a.u.)		
<100>	6.95	<100>	6.89	3830		
<100>	3.17	<100>	4.44	1900		
<100>	8.16	<100 + 221>	3.20	2020		
<100>	6.09	<100 + 221>	1.81	510		
<100>	4.71	<100 + 221>	1.37	420		
<100 + 221>	4.03	<100 + 221>	1.43	755		
<100 + 221>	2.43	<111 + 100>	1.59	790		
<100 + 221>	2.11	<111 + 100>	1.66	420		
<100 + 221>	2.10	<111 + 100>	1.69	320		
<100 + 221>	1.50	<111 + 100>	1.51	430		
<100 + 221>	1.49	<111 + 100>	1.49	180		
<100 + 221>	1.17	<110 + 100>	1.20	125		
<100 + 221>	1.27	<110>	1.28	190		
<100 + 221>	4.13	<110 + 411>	1.50	170		
<110>	1.11	<110>	1.40	150		
<110 + 411 + 877>	1.52	<110 + 411 + 877>	2.11	315		
(a.u. = arbitrary units)						

the profile is related to the coherent domain size and the Gaussian contribution to the line width arising from the microstrain.^{14,16}

For the X-ray determination of NiO content, the corrected integrated intensity of the corresponding reflex was used.¹⁷ Here it was assumed that the irradiated layer volume ≤ 0.5 mm³ was representative of the total layer volume investigated. The integrated intensities of the NiO (111) peaks were fitted to a Voigt function and the values are listed in Tables 1 to 4 in. counts (arbitrary units).

The measurements of the fiber texture and the evaluation of the preferred orientations were made according to the reflection method of Schulz¹⁸ in the tilt angle range $\chi \le 75^{\circ}$ from the reflections (111), (200) and (220). According to Bunge,¹⁹ the quantitative computation of the texture index TI, a measure of the sharpness of the texture, was found from the three measured pole figures over the orientation distribution function, ODF.¹³

Table 2 Dependence of NiO Content on Texture Development

No.	Initial Text	ure	End Text	NiO	
	Components	TI	Components	ΤI	cts (a.u.)
02	<100>	3.17	<100>	4.44	1900
06	<100 + 221>	4.03	<100 + 221>	1.43	755
07	<100 + 221>	2.43	<111 + 100>	1.59	790
14	<100 + 221>	4.13	<110 + 411>	1.50	170
(a.u. =	arbitrary units)				

Results & Discussion

In the course of the study, it was established that in heattreated Ni-Mn-S samples in air medium (20 hr, 450 °C) different quantities of NiO were formed (Fig. 1). Moreover, it was found that for the various samples, these quantities differed more than an order of magnitude and were within an interval of 125 to 3800 cts. Thus, three main groups could be identified (Table 1).

- A) Samples with very high NiO content: more than 1900 cts.
- B) Samples with average NiO content: 320 to 790 cts.
- C) Samples containing very small amounts of NiO: below 320 cts.

Under heat treating conditions, the layers from the first group do not change the texture components and the degree of texture sharpness. They have initial <100> texture with a high texture index, TI. After heat treatment, these layers contain the largest amount of NiO.

The second group layers can be divided into two subgroups: In the first, (B1) with a high texture index, the main texture components change very slightly after a heat treatment of 20 hr. The axis of the preferential orientation <100> is preserved, although the texture index TI is significantly lowered and additional texture components (*e.g.*, <221>) are formed.

As a result of heat treatment, samples from the second group (B2) which initially have a significantly lower texture index, change their texture components considerably. Together with the initial <100> axis of preferred orientation, a new <111> axis is formed. This indicates that high temperatures cause a sharp change in the number of domains oriented in the <100> direction. The NiO incorporated in samples from the second group is considerably lower in quantity (to 790 cts.) than that in group A. The lowest NiO quantities (below 320 cts.) observed in samples form the third group which, after heat treatment, have a <110> basic fiber texture.

The data in Table 1, showing the quantity of incorporated oxygen during the time of electrolysis growth, reveal that oxygen is not related to the concentration of NiO being formed at high temperatures. This means that the oxygen necessary for the formation of NiO is additionally incorporated into the layer, probably during the heat treatment.

Role of Texture on Formation of NiO

The data in Table 1 show that most probably the different textures possess different affinity for NiO formation. Accounting for the quantity of the NiO incorporated, it can be concluded that the <100> texture has the highest affinity for the formation of NiO and <110> the lowest. A correlation is observed between the reduction of the incorporated NiO and the decrease of the <100>-oriented crystallites. The geomet-



Fig. 5—Relationship between NiO content and change of microstrain $\Delta \varepsilon / \varepsilon$ only for samples not showing change of <100> texture during heat treatment.

ric or crystallographic factors may be responsible for this anisotropic oxidation at higher temperatures. A decreasing order of oxidation was observed from the different faces [e.g., (100), (111) and (110)] of a single copper crystal.²⁰

Samples with the same initial <100> texture and near initial texture index are listed in Table 2. After the heat treatment, different texture development is observed. Sample No. 2 shows a maximum content of NiO. The <100> texture remains intact during the annealing process. Sample Nos. 6 and 7 show a strong reduction of texture index as well as a reduction of NiO content. Sample No. 14 shows a total change of texture: a <110> orientation with smaller texture index and a very small amount of NiO was observed. In general, the formation of NiO is impeded through the disorientation of the <100> crystallites.

Role of Microstructural Parameters On Formation of NiO

Table 3 shows the results of texture, texture index and NiO content, domain size D and the microstrain ε before and after heat treatment. The difference $\Delta \varepsilon$ and the ratio $\Delta \varepsilon/\varepsilon$ at different temperatures are also listed in the same table. Analysis of the results shows that along with the type and degree of texture (TI), the changes of the other structural characteristics may be recognized as a second important criterion for the structural transformation occurring during recrystallization. The large difference in the values of these structural parameters for the various sample groups, before and after heat treatment, would serve as an important indication for the degree of change in the structure of the layers investigated.

Table 3 also shows that the difference between the initial and final values of the average ε , as well as their relative reduction $\Delta\varepsilon/\varepsilon$. The values are the smallest for samples from group A in which the maximum quantity of NiO is incorporated. During the annealing process, the domain size in these samples changes slightly (Sample 1, from 618 to 957 Å; Sample 2, from 485 to 984 Å), as well as the value of TI for Sample 1, for which the highest NiO quantity is determined. A relatively smaller quantity of NiO is incorporated in Samples 2 and 3, in which there is a relative change in the initial degree of preferential orientation.

More significant changes were observed for samples from group B1. Although the initial <100> texture is preserved, the size of D(Å) is changed more than one order of magnitude

Table 3

Dependence of NiO Content on Structural Parameters: Texture Components, Domain Size & Microstrain

	Texture Components								
	Initial Text	ture	End Texture						
	components	TI	components	TI					
01	<100>	6.95	<100>	6.89					
A 02	<100>	3.17	<100>	4.44					
03	<100>	8.16	<100 + 221>	3.20					
04	<100>	6.09	<100 + 221>	1.81					
B 05	<100>	4.71	<100 + 221>	1.37					
06	<100 + 221>	4.03	<100 + 221>	1.43					
07	<100 + 221>	2.43	<111 + 100>	1.59					
08	<100 + 221>	2.11	<111 + 100>	1.66					
C 09	<100 + 221>	2.10	<111 + 100>	1.69					
10	<100 + 221>	1.50	<111 + 100>	1.51					
11	<100 + 221>	1.49	<111 + 100>	1.49					

Domain Size			Microstrain				
Initial	End	Initial	End	$\Delta \epsilon$	Δε/ε	cts	
Α	Α		10 ⁻³		%	(a.u.)	
618	957	1.95	1.85	0.10	5	3830	
485	984	2.51	2.25	0.26	10	1900	
724	>2000	1.98	1.24	0.74	37	2020	
588	>2000	2.19	1.09	1.10	50	510	
507	>2000	2.34	1.06	1.28	55	420	
373	>2000	2.63	1.05	1.58	58	755	
214	>2000	3.67	1.10	2.57	71	790	
189	>2000	3.98	1.09	2.89	73	420	
196	>2000	4.01	1.06	2.94	75	320	
177	>2000	4.07	1.79	2.28	57	430	
164	>2000	4.26	1.32	2.94	70	180	
1	•, •						

(a.u. = arbitrary units)

(over 2000 Å) and it cannot be measured by X-ray methods. Subsequently, a considerable reduction of microstrain ($\Delta\epsilon$ from 1.1 to 1.6; $\Delta\epsilon/\epsilon$ approximately 55 percent) and decrease in TI take place. As mentioned above, these changes are a definite indication of a significant transformation of the initial structure and confirm the occurrence of a considerable degree of recrystallization. For these samples, the incorporated NiO quantity decreases from 420 to 755 counts.

As a result of heat treatment, the samples from group B2 change their initial <100> to <100 + 111> orientation. The domain size exceeds 2000 Å and cannot be determined by Xray methods. The reduction of the average deformation ε compared to that of the previous group is even larger ($\Delta\varepsilon$ from 2.3 to 3; $\Delta\varepsilon/\varepsilon$ approximately 70 percent), which indicates that samples of this group have stronger recrystallization processes. The quantity of NiO formation will be even smaller.

The curve between the NiO content as a function of the microstrain ε (Fig. 2) shows that there is no simple dependence of NiO formation on the structural defects. Figures 3-5, however, confirm our suggestions about the role of the change of ε with thermal treatment. There exists unambiguously a strong dependence between the amount of NiO formed and the degree of $\Delta \varepsilon$ (Fig. 3). The exponential relationship can be interpreted such that the NiO formation

Dynamics of NiO Formation after 5, 10, 20 & 30 hr Heat Treatment, With Texture Orientation, Texture Index (TI) and Amount of NiO

No. 02 Texture TI NiO (a.u.)	As Plated <100> 3.17) –	5 hr	10 hr	20 hr <100> 4.44 1900	30 hr <100> 6.62 1860
06 Texture TI NiO	<100+221> 4.03 -			<100+221>< 1.43 755	100+221> 1.58 760
08 Texture TI NiO	<100+221> 2.11 -	<100+111> 1.29 230	<111+100> 1.35 420	<111+100> 1.65 420	
10 Texture TI NiO	<100+221> 1.50 -	<100+111> 1.22 190	<111+100> 1.32 390	<111+100> 1.51 430	
13 Texture TI NiO	<100+221> 1.27 -			<110> 1.28 190	<110> 1.39 2.15
15 Texture TI NiO	<110> 1.11 -			<110> 1.4 150	<110> 1.55 170

originates from many factors. Figures 4 and 5 show correlations, therefore, between the NiO formation with $\Delta \varepsilon$ and $\Delta \varepsilon/$ ε only for samples, which do not change their <100> texture during the heat treatment (Table 1, groups A and B1). A linear relationship (r² = 0.75 and 0.77) demonstrates that the structural changes affect the NiO formation process during the thermal treatment.

From these results, it may be concluded that changes in the initial state of the deposits impedes the formation of NiO; and the amount of NiO formed is maximum when the initial state is retained. The change of microstructural parameters may be considered as a second important criterion other than texture and texture index, which can be used to characterize the recrystallization process in the deposits.

Dynamic of Heat Treatment

To obtain additional information about the ongoing processes at high temperatures, experiments were performed to study the dynamics of NiO formation, depending on the time of treatment. From the results presented in Table 4, it is clear that the main NiO quantity is formed during the first 10 hr of the heat treatment. Further heat treatment does not cause significant change in the NiO quantity. It should be emphasized that this dependence is valid for various texture types. Surely, as proved above, as a result of the different affinities for oxygen exhibited by the various textures, the absolute value of the incorporated NiO varies by more than one order of magnitude, depending on the type of texture.

The fact that the main quantity of NiO formed during the first hours of heat treatment agrees with our previous observations, reveals that the texture and its degree of texture index change in a similar way with the time of heat treatment. This analogous behavior can be regarded as an indirect confirmation of our assumption that there is a synonymous correlation between the quantity of NiO formed and the texture type.

It should be noted that in some cases, further heat treatment, although the texture index TI increases, does not alter the quantity of NiO already formed. It can be assumed, therefore, that the domains additionally oriented in the <100> crystallographic direction show increased affinity for NiO formation, but they are not able to incorporate more oxygen from the medium for further reaction to form NiO. It seems that in the first hours of heat treatment, the number of domains with this <100> orientation is decisive for NiO formation. Probably the incorporated NiO blocks further access to oxygen in the layer and the subsequent recrystallization processes cannot contribute to the additional formation of NiO.

Possible Alternative Explanation

The data discussed and the conclusions raise a significant question: Is it possible that the different quantity of NiO is not a result of the different degree of transformation of the layers having initial texture <100>, as supposed here, but is a consequence of different stability? It may be assumed that the formation of large amounts of NiO stabilize the deposits with high <100> texture index, but Sample 3 (Table 3) shows that despite large amounts of NiO with high texture index, the recrystallization process is not stopped. The structural transformation, the change of texture and microstructure, proceed at high speed. On the other hand, the content of NiO formed in the deposits with <110> texture is of no significance. These deposits (Samples 15 and 16, Table 1) remain stable with respect to the texture and microstructure. These results indicate unambiguously that the formation of NiO is the consequence and not the cause of the formation of a definite texture from high-temperature treatment.

Findings

The following main conclusions can be drawn from these investigations.

- 1. The quantity of incorporated NiO depends (a) on the texture type and the degree of perfection, and (b) on the grade of recrystallization. In this case, (b), defects and impurities make the structure even more unstable and there is an easy transformation to other textures that possess less affinity for NiO.
- 2. The formation of NiO is a consequence and not a cause of the formation of a definite texture. The results show that the processes at high temperatures are complicated. The recrystallization process cannot be understood without a detailed knowledge of structural parameters, because many other factors are involved. In this case, it is possible to develop a model about the occurring processes and mechanism. This could facilitate the solution of concrete problems of materials over a wide temperature range.

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